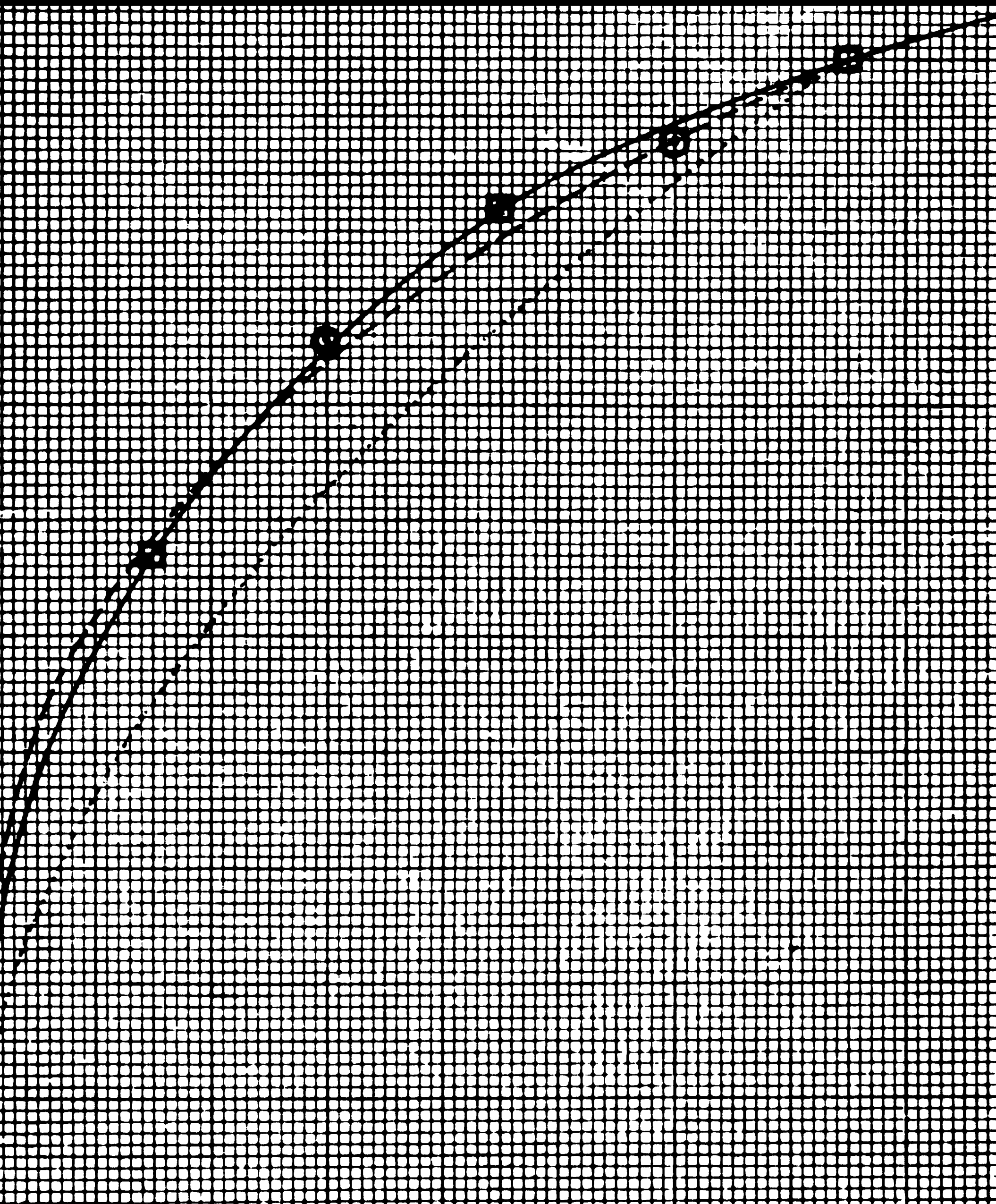

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A NEW FOSSIL CRAB FROM THE MIOCENE GREEN-SAND BED OF GAY HEAD, MARTHA'S VINEYARD, WITH REMARKS ON THE PHYLOGENY OF THE GENUS CANCER.

By Alpheus S. Packard.

WITH TWO PLATES.

PALEONTOLOGICAL NOTES, NO. V.

A NEW FOSSIL CRAB FROM THE MIOCENE GREENSAND BED OF GAY HEAD, MARTHA'S VINEYARD, WITH REMARKS ON THE PHYLOGENY OF THE GENUS CANCER.

BY ALPHEUS S. PACKARD.

Received May 8, 1900. Presented May 9, 1900.

In looking over a small collection of fossil crabs made by Mr. J. H. Clarke of Providence, R. I., about thirty years ago, there occurred one specimen which represented quite a different group from Stimpson's *Archaeoplax signifera.* It came, he told me, from the same bed and locality at Gay Head as the other crabs.

On consulting with Mr. Walter Faxon, assistant in charge of the Crustacea of the Museum of Comparative Zoölogy, who kindly showed me the fossil crabs of the collection, we concluded that though the body was very round and the surface of the carapace much more convex, it could not belong to any other genus. Mr. J. B. Woodworth also kindly allowed me to examine a trayful of fragments of Archaeoplax collected by him while connected with the U. S. Geological Survey, from the greensand bed at Gay Head. Among them was the hand of what was plainly enough that of a large Cancer, like our common *C. irroratus*, and it seemed evident that it must have belonged to a large individual of the same species as the small crab. Both still retained more or less of the greensand, and the hand was loosely embedded in a matrix of that material. For the opportunity of describing the hand, I am indebted to the U. S. Geological Survey.

Cancer proavitus, n. sp., Plate I., Figs. 1, 2, 3. One young male represented by the carapace, sternum, and basal joints of the legs. All the teeth on the front edge of the carapace absent except the two on the left side of the left orbit.

Body much narrower, and therefore rounder, more orbicular than in the existing species.

Carapace entire, with the exception of the greater part of the front margin. It is much higher and much more convex than in the two existing species of our coast (*C. irroratus* and *C. borealis*), being almost rounded, the convexity being between one-fourth and one-third the entire thickness of the body. The surface is much more irregular than in the two existing species, being thrown up into fourteen well-marked, more or less flattened, bosses or tuberosities. Of these, four are situated along the median line; the one most posterior is the broadest and highest, the fourth or most anterior one the smallest and lowest; also the granulations or crateriform papillæ covering the surface of all the tuberosities are larger and more prominent than those elsewhere on the surface of the carapace. On each side of the median row are five other flattened low tuberosities, the largest of which is opposite the second median one (counting from behind), and half-way between this and the outer side of the same tuberosities is a small one; behind the one first named is a small one situated opposite to the first (or most posterior) median tuberosity. In front there are two small tuberosities, situated opposite the anterior median one, but placed a little nearer the front edge, and directly behind the orbit or base of the eyestalk; of these two bosses the outer one is the larger.

Fortunately on the left side of the left orbit two of the marginal teeth of the carapace are perfectly preserved; they correspond to the second and third teeth, from the left orbit, of *C. irroratus*. The third tooth (corresponding to the third tooth in *C. irroratus*) is straight on the free edge, with about 15 papillæ or granulations along the edge, while the other (the second) is more conical or tooth-like, with from 16 to 18 granulations; indeed the granulations on the edge and near it are almost exactly the same in number, size, and position as in *C. irroratus*.

The hinder edge of the carapace is much as in *C. irroratus;* the row of granulations on each side of the middle of the carapace, and the shorter oblique row extending to the insertions of the hinder pair of legs, are almost exactly as in the existing species. In the fossil species there are about four of these granulations to the millimetre, there being the same number in *C. irroratus*, at a point near the median line of the carapace; while in the middle of the series there are five, but in *C. irroratus* only three, being slightly larger and farther apart.

The sternum is as in the male *C. borealis*, as are the basal joints of the legs, and I can detect no good specific differences. In the sternum of the fossil species, the three segments, including the apical one, which ends at the insertion of the maxillipeds, are well preserved.

On the posterior edge of the penultimate sternal segment are two minute tubercles, but with the tips broken off, which are exactly as in *C. irroratus;* these little tubercles we take to be the "genital tubercles" of Stimpson. The abdomen itself is wanting. The sternum is on the whole rather more like that of *C. borealis* than *C. irroratus.*

The large hand evidently belonging to this species is marked in exactly the same manner on the outer aspect as in *C. borealis*, having the four distinct raised granulated lines or ridges, with the same arrangement as in the living species. The single specimen lacks the articular face at the base, as also unfortunately the fingers, and also the spine at the base. Of the four ridges on the inner face, on the lowest ridge there are 32 papillæ, or conical granulations; on the ridge above, where they are much smaller, about 33; in the third ridge there are two rows of conical granulations, one consisting of 20 large ones, with a parallel row of minute ones below; on the fourth ridge there are about 12–14 large granulations, with smaller ones situated irregularly on the lower side, while some others are interpolated between the large ones. The concavities between the ridges are well marked.

Length of carapace, 30 mm.; width, 38 mm.

Thickness of the body in the middle, 17–18 mm.; amount of convexity of the dorsal surface of the carapace, about 5 mm.

Length of sternum, 20 mm.; greatest breadth, 12 mm.

Length of hand without the fingers, of the other specimen, 30 mm.; breadth, 21 mm.

On comparison with seven small *C. irroratus* (2 ♂ and 5 ♀) of nearly the same age, it is seen to differ markedly in three points, *i. e.*, the very narrow, much rounded, or orbicular body, the much more convex carapace, and the much greater number and prominence of the flattened tuberosities.

In the small *C. irroratus* 34 mm. long the carapace is 50 mm. in width, or 16 mm. wider; in *C. proavitus*, which is 30 mm. long, it is only 8 mm. wider than long.

In *C. irroratus* we see only traces of the tuberosities on the sides of the carapace, those of the median line being obsolete. On each side of the median line or region in *C. irroratus* are two obscurely marked tuberosities, but they are very low, broad, and flat. The most striking difference, however, is the much more rounded shape of the body. On the other hand, the teeth and granulations on the teeth, and on the narrow ridges of the posterior edge of the carapace, are nearly identical.

Comparing the hand of the fossil species from the U. S. Geological

Survey with that of a *Cancer irroratus* about four inches wide, notable differences are to be seen. Though the four ridges are the same in length, width apart, and in general arrangement, the teeth on these ridges are in *C. proavitus* very much larger, and are represented in *C. irroratus* by more numerous and crowded granulations, which are flattened, rounded, and polished.

In some important respects the tertiary species resembles *C. borealis*. This differs from *C. irroratus* in being finely muricate, the minute setiferous tubercles being much larger, higher, and sharper, almost forming sharp spines; they are also more numerous and crowded, and often bear a hair. In these respects *C. proavitus* approaches *C. borealis*. As in *C. irroratus*, the antero-lateral margins are nine-toothed; of these teeth the ninth, or that next to the orbit, is sharper than in the other living species, and ends in a sharp spine, with several accessory spinules. The postero-lateral margins are more sinuous than in *C. irroratus*, and the granulations on the ridge are larger, fewer, and end in a point. In both of the living species the convexity of the carapace is about the same. The surface in *C. borealis* is perhaps a little more uneven.

The hand of *C. borealis* differs from that of *C. irroratus* in being much more muricate or spiny, the granulations on the four external ridges of the latter being represented by well-marked sharp spines, these being especially large and high on the uppermost ridges.

C. borealis is a decidedly hairy species, whereas *C. irroratus* is naked, but a few hairs being visible; on the other hand, in *C. borealis* nearly every tubercle bears a pale hair.

The abdomen of *C. borealis* differs from that of the more common species (*C. irroratus*) in being less acute and mucronate at the tip. The sternum is a little more hairy.

Length of a small *C. borealis*, 30 mm.; breadth, 39 mm.; thickness of body, 10–11 mm.

The phylogeny of the Eastern American species of the genus Cancer. — A comparison of the miocene tertiary species of Cancer with the two species now living in the waters of Vineyard Sound, brings out the interesting fact that the extinct species appears to be the stem or ancestral form from which the recent species mentioned have descended.

Cancer proavitus presents characters in which it resembles *C. borealis* as well as *C. irroratus*. It resembles *C. borealis* in the higher, more pointed granulations on the postero-lateral margin of the carapace, and in the quite high and sharp spines on the ridges of the hand, as well as the numerous setiferous spines and hairs; on the other hand it is simi-

lar to *C. irroratus* in the shape of the nine teeth on the antero-lateral margin of the carapace, and in the straight postero-lateral margin of the same. It is rounder, narrower, the carapace more convex, and the body in general more hairy than either of the existing species.

It thus seems most probable that the miocene species, being a more generalized, composite form, is the ancestor from which either towards the end of the pliocene or the beginning of the quaternary period the two living species sprang. *C. irroratus* has inherited the exact shape of the lateral teeth, and the shape of the postero-lateral margin of *C. proavitus*, while *C. borealis* has retained the higher spine-like granulations or submuricate feature of the carapace and hand, and the hairiness of the body.

On the whole the evidence that our two northeastern species have descended from a much more rounded, convex, and hairy miocene form living in the same geographical area seems well established.

It would be most interesting to compare this fossil species with very young individuals of our living species, but after inquiry I find they are not in existence in our museums. It is to be hoped that specimens of the very young may be collected and compared with the fossil species. It is known that in Cancer the body grows wider with age.

Note on Archaeoplax signifera Stimpson.* — While the collections of the fossil Crustacea made at Gay Head comprise only one specimen of *Cancer proavitus*, with the hand of a much larger individual, the fragmentary remains of the Archæoplax are much more abundant, showing that it was the most prevalent form.

The specimens, however, in the Museum of Brown University, and those collected by Mr. Clarke, and those in the Cambridge Museum, are, so far as we have observed them, not sufficiently well preserved to enable one to make a restoration which would be a very decided improvement on the excellent diagrammatic drawings by Dr. Stimpson. None of the specimens of the carapace — and in two large specimens they are tolerably well preserved — show the four teeth of the antero-lateral margin; on the other hand, in Mr. Clarke's specimens the legs of the four posterior pairs are well enough preserved to show five of the joints, the terminal ones wanting; the fourth joints are of unusual length.

In one young specimen the carapace has been broken away on the back so as to still show the gills in place.

Regarding the temperature of the water of the miocene period at Gay

* On the fossil Crab of Gay Head, Boston Journal of Natural History, VII. No. 4, April, 1863.

Head Dr. Stimpson remarks: "The abundance of specimens of the *Archaeoplax* at Gay Head indicate a warm climate in that region at the time they were living. At the present day all Carcinoplacidæ are inhabitants of warm seas. The nearest allied genus, *Heteroplax*, lives on the coast of China at the northern limit of the torrid zone."

The occurrence of a species of Cancer in the same bed does not necessarily tend to prove that the water of the sea on our miocene coast was not somewhat warmer than at present, though not of subtropical temperature. There are four species of Cancer on the Pacific coast of North America, where *C. magister* ranges from Sitka to Monterey, *C. gracilis* from Puget Sound to San Francisco Bay, *C. productus* from Puget Sound to San Francisco, while *C. antennarius* occurs at San Francisco, Monterey, and Tomales Bay. I am indebted to Miss Mary J. Rathbun, assistant in the Smithsonian Institution, for the information that there are no tropical species of Cancer, and she has kindly sent me the following list of species of this genus exclusive of those of North America and Europe: —

C. novae-zelandiae	Lucas.	New Zealand.	
C. bellianus	Johnson.	Madeira.	
C. plebeius	Poeppig.	Chile.	
C. polyodon	"	"	
C. edwardsii	Bell.	"	
C. longipes	Bell.	"	
C. japonicus	Ortmann.	Japan	
C. pygmaeus	"	"	
C. gibbosulus	(de Haan)	"	as well as west coast N. America.
C. amphioetus	Rathbun	"	" " " " "

Of the two species now living on the shores of southern New England, the most common one (*C. irroratus*) ranges from southern Labrador to South Carolina, while *C. borealis* is rarer, more local, and has thus far only been found to extend from Nova Scotia to Vineyard Sound and No Man's Land. Both, then, appear to be on the whole boreal species.

The invertebrate fauna with which *Cancer proavitus* is associated has been enumerated by Dr. W. H. Dall.* Of twenty-two species of mollusks, about eight appear to be recent species still living in the waters of that region; among them occur such boreal forms as *Mya arenaria*, *M. truncata*, *Yoldia limatula*, *sapotella*, etc., and Dall states:

* Notes on the Miocene and Pliocene of Gay Head, Martha's Vineyard, etc. Amer. Jour. Sci. XLVIII., October, 1894, p. 296.

"It will be observed that this is a distinctly northern assemblage; any of the species might be at home in the waters about Gay Head to-day, as far as we can judge by analogy in the case of extinct species."

It would appear, then, from the evidence thus far obtained, and taking into account the abundance of Archaeoplax, that the climate of the miocene of Gay Head, or at least the temperature of the ocean, was probably somewhat warmer, but yet not greatly different from what it now is south of Cape Cod.

PLATE I. *Cancer proavitus.*

FIGURE 1. From above, nat. size.
" 2. From below.
" 3. Hand of a larger specimen.
" 4. *Archaeoplax signifera* Stm., carapace from above, nat. size.

Fig. 1

Fig. 2

Fig. 3

Fig 4

PLATE II. *Archaeoplax signifera.*

FIGURE 1. Carapace from above, nat. size.
" 2. Sterna of two individuals.
" 3. Four legs, showing the very long fourth joints.

Fig. 1

Fig. 2

Fig. 3

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ON THE THERMAL DIFFUSIVITIES OF DIFFERENT KINDS OF MARBLE.

BY B. O. PEIRCE AND R. W. WILLSON.

INVESTIGATIONS ON LIGHT AND HEAT MADE AND PUBLISHED WHOLLY OR IN PART WITH APPROPRIATIONS FROM THE RUMFORD FUND.

ON THE THERMAL DIFFUSIVITIES OF DIFFERENT KINDS OF MARBLE.

By B. O. Peirce and R. W. Willson.

Received May 4, 1900. Presented May 9, 1900.

Last year we published in the Proceedings of the American Academy of Arts and Sciences an account of some determinations of the thermal conductivities of different kinds of marble, made by the so-called "Wall Method." The horizontal bases of a rectangular prism, of height small compared with the area of a horizontal cross section, were kept for a long time at constant temperatures, the final temperatures at two or more points in the vertical axis were determined, and the flux of heat through a definite central portion of the colder base was measured. For the details of the apparatus we refer to that paper.

In each experiment of one of our sets a rectangular prism 60 cm. square and not more than 6 cm. high was built up of a slab of the material to be tested, enclosed between two other slabs of the same material. Between each two consecutive slabs of the prism was placed a thin metal sheet. This consisted of two rectangular leaves of tinfoil, about 60 cm. long and a little less than 30 cm. wide, placed side by side, and separated by a narrow ribbon thermal element made by butt-jointing, end to end, with the help of silver solder, a strip of German silver, and a strip of copper of the same thickness as the tinfoil. After the edges of the ribbon had been varnished so as to prevent electrical contact, the ribbon and the tinfoil could be placed close together so as to form a continuous sheet of metal 60 cm. square and about 1–10 of a millimetre thick.

The ribbon thermal elements gave consistent results at all times, provided that the junctions themselves were in contact with the slabs between which they lay. If the tinfoil wings were considerably thicker than the junction-ribbon, or if the junction itself were scraped thin, the reading might be in error by an amount not easy to be accounted for by the mere resistance of the thin air-film on each side of the junction.

TABLE I.

	Sp. Gr.	Conductivity.	Avg. Sp. Heat (25° to 100°).	Sp. Heat per Unit Vol.	Diffusivity.
1. Carrara	2.72	0.00505	0.214	0.579	0.0087
2. Mexican Onyx . . .	2.71	0.00556	0.211	0.572	0.0094
3. Vermont Statuary . .	2.71	0.00578	0.210	0.569	0.0102
4. American White . . .	2.72	0.00596	0.214	0.582	0.0102
5. Egyptian	2.74	0.00623	0.212	0.581	0.0107
6. Sienna	2.68	0.00676	0.215	0.576	0.0117
7. Bardiglio	2.69	0.00680	0.218	0.586	0.0116
8. Vermont Cloudy White	2.75	0.00681	0.210	0.578	0.0118
9. Vermont Dove Colored	2.74	0.00684	0.208	0.570	0.0120
10. Lisbon	2.75	0.00685	0.211	0.580	0.0118
11. American Black . . .	2.68	0.00685	0.214	0.574	0.0119
12. Belgian	2.75	0.00755	0.206	0.567	0.0133
13. African Rose Ivory .	2.75	0.00756	0.212	0.583	0.0130
14. Tennessee Fossiliferous	2.71	0.00756	0.214	0.580	0.0130
15. Knoxville Pink . . .	2.73	0.00757	0.212	0.579	0.0131
16. St. Baume	2.70	0.00761	0.210	0.567	0.0134

After the absolute conductivity of a particular specimen has been carefully determined, between various pairs of temperature limits, the conductivity of any other specimens can be easily obtained by determining the temperature-gradient, in the final state, on the axis of a prism built up of the slab already tested, and the slab to be examined, with their attendant thermopiles and such other thin slabs as may be conveniently used. By varying the order of the slabs on different occasions, the temperatures at the faces of the slab to be examined can be altered, it being always understood that the thermal elements must be placed between slabs of approximately the same conductivities. The relative conductivities of different materials, if these conductivities are not widely different, can be determined with great accuracy by this method; and it is possible to

TABLE II.

	Higher Temperature.	Lower Temperature.	Average Specific Heat.	Calculated.
1.	80.2	26.90	0.199	0.1956
2.	80.2	26.91	0.199	0.1956
3.	75.7	26,00	0.196	0.1942
4.	76.0	26.10	0.199	0.1947
5.	63.0	24.40	0.196	0.1919
6.	61.0	24.36	0.185	0.1915
7.	61.0	24.30	0.191	0.1915
8.	53.0	24.60	0.181	0.1900
9.	58.0	24.60	0.198	0.1900
10.	48.1	22.27	0.189	0.1887
11.	48.0	22.24	0.189	0.1886
12.	44.3	22.40	0.188	0.1880
13.	44.1	22.20	0.188	0.1879
14.	44.1	22.40	0.189	0.1880
15.	91.5	27.90	0.197	0.1979
16.	100.00	29.66	0.109	0.1999
17.	100.00	28.20	0.191	0.1996
18.	100.00	28.10	0.198	0.1996
19.	100.00	28.38	0.200	0.1996
20.	79.1	25.54	0.196	0.1951
21.	79.1	25.80	0.193	0.1952
22.	79.2	26.40	0.198	0.1954

use much smaller slabs than are necessary for the determination of absolute conductivities.

For many purposes to which the results of our experiments might be applied, it is desirable that the specific heats of the various marbles should

be known; this information is given in the following table. For convenience the values of the conductivities, as printed on Page 56, Volume xxxiv. of the Proceedings of the American Academy, are appended. At least two specimens of each sort of marble except No. 15 were examined.

To determine the variation of the specific heat with the temperature, the following determinations were made by the "Method of Mixtures," upon specimens of Carrara marble dried at temperatures somewhat above 100° C.

These observations are well represented by assuming the following expression for the specific heat of dry Carrara marble: —

$$S = 0.1844 + 0.000379\ t^2$$

The fifth column of the above table gives the values of the mean specific heat between the given temperatures computed by the formula $Q = 0.1848\ (t - 25°) + .0001895\ (t - 25°)^2$ where Q is the quantity of heat in calories required to raise 1 gr. from 25° to the temperature t: this expression corresponds to the equation above given for S.

The 17th observation was marked for rejection, a piece of the substance having been dropped from the cup in which it was heated and hastily picked up and dropped into the calorimeter. As it is difficult to believe that this accident could cause so great a difference in the result as appears, we have thought it best to retain the observation.

JEFFERSON PHYSICAL LABORATORY, CAMBRIDGE,
February, 1900.

Proceedings of the American Academy of Arts and Sciences.

VOL. XXXVI. NO. 3.—JULY, 1900.

GEOMETRY ON RULED QUARTIC SURFACES.

BY FRANK B. WILLIAMS.

GEOMETRY ON RULED QUARTIC SURFACES.

BY FRANK B. WILLIAMS,
FELLOW IN MATHEMATICS, CLARK UNIVERSITY, MASS.

Presented by William E. Story, May 9, 1900.

I. INTRODUCTION.

1. RULED quartic surfaces have been studied systematically by Cayley, Cremona, and Salmon, and to some extent by Rohn, Chasles, Schwartz, Reye, Voss, Holgate, and others. Of the quartic scrolls, Cremona,* in his excellent synthetic treatment, enumerates twelve species, while Cayley,† in the most complete and masterly analytical treatment of scrolls, divides these scrolls into ten species and gives a comparison of his species with those of Cremona, stating that the latter's two remaining species, though properly considered as distinct from the others, may be regarded as sub-forms of his seventh and ninth species. As we shall not have occasion here to take account of these sub-forms, we shall follow Cayley's classification. The other ruled quartic surfaces are: the developable quartic, or *torse*, whose edge of regression is a twisted cubic, and the quartic cones, which, although developable, must be considered separately. The developable quartic has been quite thoroughly studied by Cayley, Salmon, and others, but very little seems to have been done with the quartic cones, which, as will appear later, present some very interesting features.

The consideration of curves in space has been the subject of a great many articles by the most eminent geometricians, but curves on ruled quartic surfaces in particular have received little attention. As early as 1861, Chasles ‡ gave a method of describing curves of order $4m + n$, on

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* Sulle superficie gobbe di quarto grado, Mem. della R. Istoria di Bologna, Series II., T. VIII.

† Second and Third Memoirs on Skew Surfaces, Otherwise Scrolls. Coll. Math. Papers, Vol. V. and Vol. VI., respectively, and Phil. Trans., 1863 and 1869, respectively.

‡ Description des courbes à double courbure de tous les ordres sur les surfaces réglées du troisième et du quatrième ordre. C. R. LIII, 884–889.

ruled quartic surfaces, by means of a pencil of surfaces of order m and groups of n generators in involution. In 1897, Rohn * treated some of the properties of curves on the general quartic surface, considering also the surfaces that can be passed through these curves and presenting some theorems regarding the residual intersection.

In 1883, Professor Story discovered a method by means of which he was able to classify all curves lying on a quadric surface and to give a formula for the number of intersections of these curves, thus obtaining, by a synthetic process, the results already found by Cayley.† Professor Story applied his method to the cubic scrolls, classifying all curves lying on these surfaces and obtaining a formula for the number of intersections of any two of these curves, analogous to that found for curves on quadrics.

By an extension of the analytical method of Cayley, Dr. Ferry ‡ succeeded most admirably in treating analytically the "Cubic Scroll of the First Kind," verifying the results of Professor Story for this surface, and in a paper soon to be published, Dr. Ferry has also verified, in the same way, Professor Story's results for the other cubic scroll.

It is the purpose of the present paper to consider the classification of curves on all ruled quartic surfaces; to find the formula for the number of intersections of any two curves that lie on the same ruled quartic surface; and to point out some of the most notable results obtained in the course of the investigation. The equations of many of the ruled quartic surfaces are so complicated that very serious difficulties arise when we attempt to treat them analytically, and it has been found most convenient to employ the synthetic method of Professor Story.

2. For convenience, we shall use the symbol $S^{(\nu)}$ to denote a surface of order ν, and $\Sigma^{(\mu)}$ to denote a ruled surface of order μ. $C^{(a)}$ will be used to denote a curve of order a lying on the ruled surface in question. By an arbitrary generator we shall mean any simple generator that bears no special relation to the curve in question, e. g. in considering a plane curve, it is any simple generator not lying in the plane of the curve. It must be proved, first of all, that every curve $C^{(a)}$ meets each generator of the surface on which it lies in a constant number of points, say

* Die Raumcurven auf den Flächen IV[ter] Ordnung. Verhandlungen der K. Sächs. Gesell. der Wiss. zu Leipzig, 1897.

† On the curves situate on a surface of the second order. Coll. Math. Papers, Vol. V., and Phil. Mag., 1861, pp. 35–38.

‡ Geometry on the Cubic Scroll of the First Kind. Archiv for Mathematik og Naturvidenskab, B. XXI. Nr. 3, 1899.

a points, equal to the number in which it meets an arbitrary generator. (If the curve goes through a point common to all the generators, e. g. the vertex of a cone, this point is not counted as one of the a points on any generator.) This furnishes us a method for classifying all curves on $\Sigma^{(\mu)}$, and we shall use the symbol a_α to denote a curve of order a that meets each generator of the surface on which it lies in α points, α being a constant. Similarly, b_β will denote a curve of order b that meets each generator β times. Each generator is itself a plane curve of order 1, and since it is not met by any other generator except those lying in its plane, it is represented by 1_0. In case $\Sigma^{(\mu)}$ has more than one system of rulings, the lines of one system are chosen as the generators, with reference to which the classification is made for all curves on that surface, and the lines of any other system are regarded simply as curves of order 1.

We shall use the symbol (a_α, b_β) to represent the number of intersections of any two curves a_α and b_β on the ruled surface.

Professor Story * proved that for all curves lying on a quadric surface $(a_\alpha, b_\beta) = a\,\beta + b\,\alpha - 2\,\alpha\,\beta$, and for all curves lying on the cubic scrolls $(a_\alpha, b_\beta) = a\,\beta + b\,\alpha - 3\,\alpha\,\beta$, and stated that it is probably true that $(a_\alpha, b_\beta) = a\,\beta + b\,\alpha - \mu\,\alpha\,\beta$, for curves on a scroll of any order μ. It will be proved here that the formula is true for all ruled quartic surfaces, i. e. that we have

(1) $$(a\,, b_\beta) = a\,\beta + b\,\alpha - 4\,\alpha\,\beta,$$

and when we say that this formula holds for a certain curve we shall mean that it gives the number of intersections of this curve with any other curve on the scroll. It must be borne in mind that these formulæ for the *cones* of different orders give, in each case, the number of intersections of the curves aside from those at the vertex, since the vertex is not one of the α points on any edge. This will be proved for the quartic cones.

3. We shall first consider three general theorems,† which must be proved before the formula can be established. The first may be called the *fundamental theorem* and may be stated thus:

Theorem I. — If α be the number of points of $C^{(a)}$ on an arbitrary generator, there are α points of $C^{(a)}$ on each generator.

* On the Number of Intersections of Curves Traced on a Scroll of any Order. Johns Hopkins University Circulars, August, 1883.

† These theorems were given by Dr. Story in his lectures, October to December, 1899.

No general proof of this theorem has yet been found, and it must be proved for each of the ruled surfaces, separately.

From Theorem I are readily deduced the other two theorems, as follows:

Theorem II. — If a_a is the complete intersection of $\Sigma^{(\mu)}$ and $S^{(\nu)}$, and if b_β is any curve on $\Sigma^{(\mu)}$ that has no component in common with a_a, then $(a_a, b_\beta) = a\,\beta + b\,a - \mu\,a\,\beta$.

Proof. — The intersections of a_a and b_β are simply the intersections of $S^{(\nu)}$ and b_β and are in number equal to $b\,\nu$, i. e. $(a_a, b_\beta) = b\,\nu$. Now since each generator meets $S^{(\nu)}$ in ν points, $a = \nu$, also $a = \mu\,\nu = \mu\,a$, and we have

$$a\,\beta + b\,a - \mu\,a\,\beta = \mu\,a\,\beta + b\,\nu - \mu\,a\,\beta = b\,\nu;$$

therefore $$(a_a, b_\beta) = a\,\beta + b\,a - \mu\,a\,\beta.$$

Theorem III. — If a_a is irreducible and the partial intersection of $\Sigma^{(\mu)}$ and $S^{(\nu)}$, $a'_{a'}$ being the residual intersection, and if the formula holds for each irreducible component of $a'_{a'}$ with an arbitrary curve b_β on $\Sigma^{(\mu)}$, it also holds for a_a with b_β.

Proof. — The residual $a'_{a'}$ may break up into several curves, but b_β, being arbitrary, does not in general contain any part of the intersection of $\Sigma^{(\mu)}$ and $S^{(\nu)}$. If $a'_{a'}$ is reducible, the order a' is the sum of the orders of the component curves, and the number of points a' in which any generator meets $a'_{a'}$ is the sum of the numbers of points in which this generator meets the component curves. Since the complete intersection of $\Sigma^{(\mu)}$ and $S^{(\nu)}$ is $a_a + a'_{a'}$ we have, by Theorem II,

$$(a_a + a'_{a}, b_\beta) = (a + a')\,\beta + b\,(a + a') - \mu\,(a + a')\,\beta.$$

By supposition

$$(a'_{a}, b_\beta) = a'\,\beta + b\,a' - \mu\,a'\,\beta.$$

Now the number of points in which b_β meets the complete intersection less the number in which it meets $a'_{a'}$ must be the number of points in which it meets a_a; therefore

$$(a_a, b_\beta) = a\,\beta + b\,a - \mu\,a\,\beta.$$

Corollary. — If the complete intersection of $\Sigma^{(\mu)}$ and $S^{(\nu)}$ consists of two curves and the formula holds for one of these curves it holds for the other also.

4. In order then to prove the formula for any $\Sigma^{(\nu)}$ it suffices first to prove Theorem I, and then to show that every curve on $\Sigma^{(\mu)}$ can be cut out by an $S^{(\nu)}$ such that the residual is a curve, or is composed of curves,

for which the formula holds. Now the formula holds for every generator, i.e. for a 1_0, since 1_0 meets b_β in β points, and the formula gives $(1_0, b_\beta) = 1.\beta + b.0 - \mu.0.\beta = \beta$. Therefore, if every conic can be cut out by an $S^{(\nu)}$ such that the residual is nothing but generators, if every cubic curve can be cut out by an $S^{(\nu)}$ such that the residual consists entirely of conics or generators or both, and in general, if every a_a on $\Sigma^{(\mu)}$ can be cut out by an $S^{(\nu)}$ such that the residual * is of order less than a or is composed of curves of orders less than a, the formula is true.

5. For certain species of $C^{(a)}$'s it may be possible to choose ν smaller than for certain other species, e.g. all the quartic curves lying on a quadric surface can certainly be cut out by cubic surfaces, but the "quartics of the first kind" can also be cut out by quadric surfaces.

We shall first determine the lowest value of ν for which we can be certain that an $S^{(\nu)}$ will cut out any species of $C^{(a)}$. This can be done for a surface of any order, μ, without difficulty, but since we are here going to treat the ruled quartics only, we shall consider the case of $\mu = 4$ only.

$S^{(\nu)}$ is determined by $\frac{1}{6}(\nu + 1)(\nu + 2)(\nu + 3) - 1$ arbitrary points.† When $\nu \geqq 5$ we must take care that $S^{(\nu)}$ does not break up into $\Sigma^{(4)}$ and a surface of order $\nu - 4$, i.e. of the points necessary to determine $S^{(\nu)}$ we must take one more than enough to determine a surface of order $\nu - 4$ as not lying on $\Sigma^{(4)}$; also, we must take $a\nu + 1$ points of $S^{(\nu)}$ on $C^{(a)}$ in order that $S^{(\nu)}$ may contain this curve; so that for $\nu \geqq 5$ the number of arbitrary points of $\Sigma^{(4)}$ through which we can make $S^{(\nu)}$ pass is

$$(2) \quad \ldots \frac{1}{6}(\nu+1)(\nu+2)(\nu+3)-1-\frac{1}{6}(\nu-3)(\nu-2(\nu-1)-(a\nu+1) = 2\nu^2 - a\nu.$$

For $\nu = 4$ we must take one point of $S^{(\nu)}$ not lying on $\Sigma^{(4)}$, but then the term $\frac{1}{6}(\nu - 3)(\nu - 2)(\nu - 1) = 1$; for $\nu = 1, 2,$ or 3 we do not have to take any points of $S^{(\nu)}$ off $\Sigma^{(4)}$, but then the term $\frac{1}{6}(\nu - 3)(\nu - 2)(\nu - 1) = 0$; therefore formula (2) gives the number of arbitrary points for all values of ν, when $\mu = 4$. We have, therefore, $2\nu^2 - a\nu \geqq 0$, which gives at once $\nu \geqq \frac{a}{2}$; so that, for the lowest value of ν, we have $\nu = \frac{a}{2}$ when a is even, and $\nu = \frac{a+1}{2}$ when a is odd. In some cases it has been found more convenient, and apparently necessary, to take ν

* The letter r, when used, shall always denote the order of the total residual.

† Salmon's Geom. of Three Dimensions, Chap. XI.

greater by one than this lowest value, in order to be able to make the residual consist of curves of orders less than a.

In determining the number of points at our disposal, given by formula (2), we have said nothing about multiple points on $C^{(a)}$, but have supposed that the points of $S^{(\nu)}$ that had to be taken on $C^{(a)}$ were ordinary points on this curve, and we shall always consider ν chosen without regard to multiple points on $C^{(a)}$. If a surface be made to pass through an ordinary point of a curve it meets the curve once at that point, and therefore we have to make $S^{(\nu)}$ pass through $a\,\nu + 1$ ordinary points of $C^{(a)}$ in order to make $S^{(\nu)}$ contain $C^{(a)}$; but if $C^{(a)}$ has a double point, any surface through this double point will meet the curve twice there, and therefore, if we make $S^{(\nu)}$ pass through this double point (which counts for only one point in the determination of $S^{(\nu)}$), we have to make it pass through only $a\,\nu - 1$ other ordinary points of $C^{(a)}$ in order to make it contain $C^{(a)}$, since $C^{(a)}$ will then intersect $S^{(\nu)}$ in $a\,\nu - 1 + 2 = a\,\nu + 1$ points. Consequently, when $C^{(a)}$ has a double point, only $a\,\nu$ of the points necessary to determine $S^{(\nu)}$ need be taken on $C^{(a)}$ if we take the double point to be one of these: this is one less than the number of points of $S^{(\nu)}$ taken on $C^{(a)}$ in deducing formula (2), above; and therefore, when $C^{(a)}$ has a double point, we shall have at our disposal one point more than the number given by formula (2). In like manner, if $C^{(a)}$ has an m-tuple point, a surface $S^{(\nu)}$ through that point meets $C^{(a)}$ m times there, and we need only make $S^{(\nu)}$ pass through $a\,\nu - (m - 1)$ other ordinary points in order that it shall contain $C^{(a)}$; and, consequently, when $C^{(a)}$ has an m-tuple point, we shall have at our disposal $m - 1$ points more than the number given by formula (2).

In accordance with this principle, it is evident that, if $\nu + 1$ branches of $C^{(a)}$ meet any line L* (i. e. if $\nu + 1$ of the points of intersection of

* It is necessary to observe here a very important fact, which is often overlooked, viz., if a curve has an m-tuple point P and the m tangents to the curve at P all lie in the same plane, a surface on which the curve lies may have this point P as an ordinary point, and any line L through P, that does not lie in the tangent plane, meets this surface only once at P; but there are m branches of the curve that meet L at P and a plane through L meets the curve m times at P. In general, if the m tangents at P do not all lie in the same plane, P will be a multiple point on any surface that contains the curve, the multiplicity k of P on any such surface being at least equal to the order of the cone of lowest order that can be passed through the m tangents, and this lowest order is always less than m. Then any line L that does not lie on the tangent cone to the surface at P meets the surface only k times at P, while any edge of the cone meets the surface $k + 1$ times there.

$C^{(\alpha)}$ with an arbitrary plane through the line L lie on L), we can then make L lie on the surface $S^{(\nu)}$ that cuts out $C^{(\alpha)}$ and still have left at our disposal the number of points given by formula (2). For, if the $\nu+1$ points of $C^{(\alpha)}$ on L are all ordinary points, L meets $S^{(\nu)}$ $\nu+1$ times and therefore lies on $S^{(\nu)}$; but, if $C^{(\alpha)}$ has an m-tuple point and $\nu-m+1$ other points on L, even if L meets $S^{(\nu)}$ only once at this multiple point, $m-1$ points not included in formula (2) are still at our disposal and may be taken on L, so that $\nu+1$ points of $S^{(\nu)}$ lie on L and L will therefore lie on $S^{(\nu)}$. Therefore, in considering whether a line can be made to lie on $S^{(\nu)}$ or not, we need not take account of the multiple points of $C^{(\alpha)}$ that lie on this line, but may regard the line as meeting $S^{(\nu)}$ in points of $C^{(\alpha)}$ equal in number to the number of points on the line in which an arbitrary plane through the line meets $C^{(\alpha)}$.

6. We have seen that, when certain theorems can be proved, formula (1), p. 21, gives the number of intersections of any two curves on the same ruled surface. In special cases, where the curves bear a particular relation to one another, and in most cases where the multiple curve is involved, the result given by this formula requires a special interpretation, namely: if two curves on $\Sigma^{(4)}$ pass through the same point of the multiple curve, any branch of either curve is regarded as intersecting only those branches of the other curve that lie on the same sheet with it, and two branches that pass through the same point of the multiple curve are not regarded as intersecting at that point if they lie on different sheets of $\Sigma^{(4)}$ there. In particular, two generators through the same point of the multiple curve are not regarded as intersecting, when considered as loci on that quartic surface.

The double curve on a ruled quartic cannot be of order greater than three, and therefore a plane section can never have more than three double points on the double curve. If the plane section has a double point not on the double curve, this double point is a point of tangency of the plane, and, since a tangent plane to a ruled surface contains the generator through the point of tangency, the section must be a degenerate quartic curve having at least one generator as a component. Therefore the section of a ruled quartic by a plane can never consist of two proper conics; for the section would then have four double points, one of which must be a point of tangency of the plane, and therefore the plane would cut out a generator.

Cayley * uses the general symbol $S(m, n, p)$ to denote a scroll gener-

* Second Memoir on Skew Surfaces, Otherwise Scrolls. Coll. Math. Papers, Vol. V., and Phil. Trans., 1863.

ated by a line that meets each of three curves of orders m, n, and p once, $S(m^2, n)$ to denote a scroll generated by a line that meets a curve of order m twice and a curve of order n once, and $S(m^3)$ to denote a scroll generated by a line that meets a curve of order m three times. In his symbols for the quartic scrolls he has also used a subscript, in most cases, to denote the order of multiplicity of the curve on the scroll; but he has not, in all cases, adhered to his general method, and it seems best, while preserving his classification, to change his symbols, making them conform to his general rule for such symbols.

II. Quartic Scroll, with a Triple Linear Director and a Simple Linear Director, $S(1_3, 1, 4)$. (Cayley's Third Species, $S(1_3, 1, 4)$.)

1. This scroll has three sheets through the triple linear director, which we shall denote by T, and T is scrolar * on each sheet.

Through each point of T pass three generators, one on each sheet, and if we pass a plane through two of these generators it will also contain the simple director, since each generator meets the simple director once, and therefore the third generator at the point lies in this same plane, for it meets it once at the point and once on the simple director; i. e. any plane through the simple director meets the scroll in this director and in three generators that intersect in the point where the plane meets T.

2. *Proof of Theorem I.* — Pass a plane through T; it meets the scroll in T and one generator and meets $C^{(a)}$ in a points. Now if we revolve the plane about T it will cut out, in succession, each generator of the scroll, and since the plane always meets $C^{(a)}$ in the same number of points, say τ points, on T, it meets $C^{(a)}$ in the same number of points, say α points on each generator, where $\tau + \alpha = a$. Since three generators lie in a plane $\alpha \overline{\overline{<}} \frac{a}{3}$ and $\tau \overline{\overline{>}} \frac{2a}{3}$.

3. *Plane Curves.* — A plane that does not pass through any line on the scroll, i. e. an arbitrary plane, meets the scroll in a plane quartic curve having a triple point on T, and since an arbitrary generator meets the plane once, every plane quartic is a 4_1.

A plane through one and only one generator cuts out a plane cubic having a double point on T, through which the generator passes, making

* Cayley calls a line *scrolar* on a surface when the tangent plane to the surface is different at each point along the line.

a triple point on the complete intersection; the generator meets the cubic again where the plane is tangent to the scroll. Since an arbitrary generator meets the plane once and does not meet the generator lying in that plane, it meets the plane cubic once, and therefore every plane cubic is a 3_1. If a plane cuts out a proper conic, it must also cut out another conic, which must be an improper conic consisting of two lines through a point of the proper conic, since the section by the plane must have a triple point on T; but the only lines on the scroll that pass through a point of T, besides T itself, are generators, and we have seen that a plane through two generators also cuts out a third generator and the simple director; therefore, there are no conics on this scroll. The triple director T is met once by each generator, and is, therefore, a 3_1. The simple director is met once by each generator, and is, therefore, a 1_1.

Each of these plane curves is either the complete intersection of the scroll and a plane, or else the residual intersection consists entirely of generators, and therefore by Theorems II and III, formula (1) holds for every plane curve on the scroll.

A plane quartic has a branch on each sheet where it crosses T, and therefore meets T three times, as the formula shows,

$$(4_1, 3_1) = 4 + 3 - 4 = 3.$$

A plane cubic has a branch on each of two sheets where it crosses T, and therefore meets T twice, $(3_1, 3_1) = 3 + 3 - 4 = 2$. The simple director does not meet T, $(1_1, 3_1) = 1 + 3 - 4 = 0$. The simple director meets a plane once, and therefore meets a plane quartic once, $(1_1, 4_1) = 1$, but since it meets each generator once, it cannot meet a plane cubic, $(1_1, 3_1) = 0$. Two plane cubics intersect in two points, on the line of intersection of their planes, $(3_1, 3_1) = 3 + 3 - 4 = 2$, the other two points, where this line meets the scroll, being the two points where each cubic is met by the generator that lies in the plane of the other. A plane cubic and a plane quartic intersect in three points on the line common to their planes, $(3_1, 4_1) = 3 + 4 - 4 = 3$, the fourth point where this line meets the scroll being the point where the generator in the plane of the cubic meets the plane quartic. Two plane quartics meet in four points on the line of intersection of their planes, $(4_1, 4_1) = 4 + 4 - 4 = 4$.

4. *Twisted Cubic* 3_1. — We saw that when a is odd we can take $\nu = \dfrac{a+1}{2}$; so, for the twisted cubic, $\nu = 2$, and by formula (2), p. 23, we have two points at our disposal in the determination of this quadric,

$S^{(2)}$, that cuts out the cubic. Since $\alpha \overline{\overline{<}} \frac{a}{3}$ we have $\alpha = 1$, and every twisted cubic is a 3_1; therefore $\tau = 3 - 1 = 2$, i. e. the twisted cubic meets T in two points, which must be distinct, since a twisted cubic cannot have a double point. Therefore the quadric that cuts out the twisted cubic meets T in two points on this curve, and since we can make the quadric pass through any two points we please that are not on the curve, we can make it pass through another point of T, and it will then contain T. The residual intersection, which is of order 5, then consists of T, which counts for three lines, and two generators, since there are no conics on the scroll, and, moreover, each generator meets the quadric once on T and once on the twisted cubic, and cannot meet it again without lying on it; and if a conic or the simple director formed part of the residual, an infinite number of generators would lie on the quadric, which is impossible. Since formula (1) holds for T and the generators, by Theorem III it holds for every twisted cubic.

A plane through the simple director cuts out three generators and meets the twisted cubic three times, once on each generator, and therefore the twisted cubic does not meet the simple director.

5. *Twisted Quartic*, 4_1. — We have $a = 4$, $\nu = \frac{a}{2} = 2$, and $r = 4$, where r is the order of the residual; $\alpha = 1$, and every twisted quartic is a 4_1. Hence $\tau = 3$, and if the quartic has no double point on T there must be three distinct points of the curve on T, i. e. T meets the quadric that cuts out the quartic three times, and therefore lies on it. If the quartic has a double point on T, it is a "quartic of the first kind," and we can pass a quadric through it and through any arbitrary point not on the curve; the quadric already meets T twice on the quartic curve, and if we make it pass through another point of T, T will lie entirely on it. In any case, the twisted quartic can be cut out by a quadric such that the residual will consist of T and one generator, and, since formula (1) holds for T and all generators, it holds for every twisted quartic; if T lies on the quadric the simple director cannot form part of the residual, since each generator already meets the quadric once on T and once on the twisted quartic. The twisted quartic has a point on each generator, and therefore meets the simple director once, $(4_1, 1_1) = 1$.

6. *Twisted Curves, in general.* — When a is odd we take $\nu = \frac{a+1}{2}$, whence $r = a + 2$; and when a is even we take $\nu = \frac{a}{2}$, whence $r = a$. We saw that $\alpha \overline{\overline{<}} \frac{a}{3}$ and $\tau \overline{\overline{>}} \frac{2\,a}{3}$ where τ is the number of points on T,

in which a_a is met by a plane through T. For $a = 3$, we saw that T could be made to lie on $S^{(2)}$, the quadric that cuts out the twisted cubic. Now for $a > 3$, $\nu = \dfrac{a+1}{2} < \tau$ when a is odd and $\nu = \dfrac{a}{2} < \tau$ when a is even. It follows at once, therefore, from what was said on p. 24, that we can always make T lie on $S^{(\nu)}$. Therefore when a is odd the residual can be made to consist of T and a curve of order $r - 3 = a - 1$, and when a is even the residual can be made to consist of T and a curve of order $r - 3 = a - 3$. Therefore, by Theorem III, if formula (1) holds for every curve of order less than a, it holds for every curve of order a; but we have proved that it holds for all plane curves and for all twisted curves of orders 3 and 4; it therefore holds for every curve of order 5 and therefore for every curve of order 6 and so on, and it therefore holds for every curve on the scroll.

7. The above proof is also applicable to the *Quartic Scroll, with a two-fold* 3 (+1) *-tuple linear director,* $S\,(\overline{1_3, 1}, 4)$. (*Cayley's Sixth Species.*) This scroll is, in fact, the limiting case of the scroll just considered, where the simple director has moved up into coincidence with the triple director. Cayley denotes this symbolically by drawing a bar over the two 1's.

The triple linear director on this scroll is torsal along one of the three sheets through it, i. e. the tangent plane to this sheet, along this director, is the same for every point of this director; the generator, lying on this sheet, that is cut out by this tangent plane, coincides with the simple linear director, and is regarded as intersecting the triple linear director at the point where the other two generators cut out by this tangent plane, one on each sheet, intersect.

III. Quartic Scroll, with a Triple Linear Director, $S\,(1_3, 2, 2)$. (Cayley's Ninth Species, $S\,(1_3)$.)

1. The triple director, T, is scrolar on each of the three sheets that pass through it, and this scroll differs from the Quartic Scroll $S\,(1_3, 1, 4)$ in not having a simple linear director, in consequence of which we have, on this scroll, three generators through each point of T that do not lie in the same plane. The plane of any two of these three generators meets the scroll otherwise in a conic that passes through their point of intersection on T, making up the triple point of the complete intersection. Therefore, there are three conics through each point of T, one in each of the three planes that contain two generators through the point.

The proof of *Theorem I* is the same as for the Quartic Scroll $S\,(1_3, 1, 4)$, p. 26. Since two generators lie in a plane, $a \overline{\overline{<}} \frac{a}{2}$.

2. *Plane Curves.* — As before, each plane curve is met once by an arbitrary generator, i. e. $a = 1$ for any plane curve. There is no 1_1 on this scroll. Each conic is a 2_1, the triple director T is a 3_1, and the other plane curves, 3_1 and 4_1, are the same as for the Quartic Scroll $S\,(1_3, 1, 4)$. Every plane curve is either the complete intersection of the scroll by its plane or else the residual is composed of generators, and therefore, by Theorems II and III, formula (1) holds for every plane curve.

Two conics do not intersect; even if they pass through the same point they lie on different sheets, and cannot be regarded as intersecting on the scroll; the formula gives $(2_1, 2_1) = 2 + 2 - 4 = 0$; the line of intersection of the planes of the two conics meets the scroll in the four points where the two generators in the plane of either conic meet the other conic. In the plane of a conic each of the two generators that lie in that plane meets the conic on T and at one other point where the plane is tangent to the scroll; therefore the plane of every conic is a double tangent plane to the scroll. T meets each conic once, $(3_1, 2_1) = 3 + 2 - 4 = 1$. A conic meets a plane cubic once, $(2_1, 3_1) = 1$, and meets a plane quartic twice, $(2_1, 4_1) = 2 + 4 - 4 = 2$.

3. *Twisted Curves.* — Since $a \overline{\overline{<}} \frac{a}{2}$, we have for the twisted cubic $a = 1$ and $\tau = 2$, where τ is the number of points of intersection of the curve and an arbitrary plane through T that lie on T. By the same reasoning as that employed on page 28, we see that T can be made to lie on the quadric that cuts out the twisted cubic, and that formula (1) holds for every twisted cubic.

When a is odd we take $\nu = \frac{a+1}{2}$. Then, since two generators lie in a plane and a is an integer, $a \overline{\overline{<}} \frac{a-1}{2}$ and $\tau \overline{\overline{>}} \frac{a+1}{2}$; but by formula (2) we have $\frac{a+1}{2} = \nu$ points at our disposal in the determination of $S^{(\nu)}$ and therefore we can make T lie on $S^{(\nu)}$; the residual will then consist of T and a curve of order $r - 3 = a + 2 - 3 = a - 1$.

When a is even we take $\nu = \frac{a}{2}$; $a \overline{\overline{<}} \frac{a}{2}$ and $\tau \overline{\overline{>}} \frac{a}{2}$. If $a < \frac{a}{2}$, $\tau > \frac{a}{2}$, i. e. $\tau > \nu$, and it follows from what was said on page 24 that T can be made to lie on $S^{(\nu)}$; the residual will then consist of T and a curve of order $a - 3$. If $a = \frac{a}{2} = \nu$, every generator meets $S^{(\nu)}$ in ν points, which

are points of a_a; if, then, any generator meets $S^{(\nu)}$ in an additional point it must lie on $S^{(\nu)}$, and therefore if any generator has on it a point of the residual it lies on $S^{(\nu)}$ and is itself a part of the residual; therefore, when $a = \frac{a}{2}$ the residual consists entirely of generators which are a in number, since the residual is of order a; and if the curve has no multiple points on T, there are $\frac{a}{2}$ pairs of generators that pass through the $\frac{a}{2}$ points where a_a meets T.

We have shown then that every twisted curve of order a can be cut out by an $S^{(\nu)}$ such that the residual will consist of curves of orders less than a, and it therefore follows, as on page 29, that formula (1) holds for every curve on the scroll.

IV. Quartic Scroll, with two Double Linear Directors and with a Double Generator, $S(1_2, 1_2, 2)$. (Cayley's Second Species, $S^{\text{v}}(1_2, 1_2, 4)$.)

1. Let us call the double linear directors D and D'; they do not intersect, and a plane through either of them cuts out also two generators that intersect in the point where the plane meets the other director, i. e. any generator A meets a definite generator B on D and another definite generator E on D', so that A and B lie in a plane through D' and A and E lie in a plane through D, while B and E do not meet. In a special form of this scroll four generators may form a gauch-quadrilateral having two vertices on each double director, e. g. taking the generators above, if A and B meet D at the point P, A and E meet D' at the point R, B meets D' at the point S, and E meets D at the point Q, the scroll may be of such a form that a generator F will pass through Q and S, as can easily be shown analytically. It is also very probable that there are special forms of this scroll on which any even number of generators, greater than four, form a gauch-polygon, but it is not the purpose of this paper to discuss these special forms. The double generator, which we will denote by G, arises from the fact that the plane quartic directing curve has three double points, one on each of the double directors and one through which G passes; a plane through G and either double director does not meet the scroll again.

2. *Proof of Theorem I.* — On any quartic scroll where the double curve is a twisted cubic, either proper or degenerate, we can prove Theorem I by passing a quadric through this twisted cubic. In the

present case the twisted cubic is degenerate, consisting of D, D', and G. Let us pass a quadric through eight points, three on D, three on D', one on G, and one on any generator A, the last two points not being on D or D'; then D, D', G, and A will all lie on the quadric and count for 7 lines in the intersection of the scroll and quadric, and therefore the quadric cuts out one more generator; the quadric passes through eight fixed points and we can make it pass through an arbitrary ninth point, so if we vary this ninth point continuously the quadric will cut out, in succession, each generator of the scroll. Now $C^{(a)}$ meets the quadric in $2a$ points, of which a fixed number lie on D, D', G, and A, and therefore the same number of points of $C^{(a)}$, say α points, lie on each generator. It is evident that there must be α points on A, for if any other generator be chosen, through which the quadric is always to pass, then there is the same number of points, α, on A, as on each of the other generators. Since we can pass a plane through D and two generators, there are $a - 2\alpha$ points of a_α on D, and, similarly, there are $a - 2\alpha$ points of a_α on D'. A plane through D and G meets the scroll in these two lines only, and there are, therefore, 2α points of a_α on G, as is otherwise evident from the fact that G counts for two generators. Since a twisted curve of order a cannot have a points on any line, $2\alpha < a$ or $\alpha < \frac{a}{2}$ for every twisted curve on the scroll.

3. *Plane Curves.* — Each double director is met once by any generator and is therefore a 2_1. No generator can meet G; for, suppose a generator A does meet it; then A meets either D or D' in a point different from that in which G meets it, and therefore the plane through G and A contains also D or D', making the order of the complete intersection of the plane and scroll as great as 5, which is impossible. G is therefore a 2_0. Then any plane through G, that does not contain D or D', meets the scroll in a proper conic that does not meet either double director, since the section has only a double point on each double director; since each generator meets the plane once and does not meet G, each conic is a 2_1, and the conics and D and D' are the only curves on the scroll for which $\alpha = \frac{a}{2}$. A plane through one and only one generator cuts out a plane cubic, a 3_1, having a double point on G and passing once through the two points where the generator in the plane meets D and D'; the generator meets the cubic again where the plane is tangent to the scroll. A plane that does not contain a line of the scroll cuts out a plane quartic, a 4_1, having three double points, one on G and one on each

double director. Every plane quartic is the complete intersection of its plane and the scroll, and therefore formula (1) holds for it (Theorem II). A plane cubic is cut out by a plane through a single generator, and D and D' are cut out by planes through two generators, and therefore, by Theorem III, formula (1) holds for every plane cubic and for D and D'. We can cut out G by a plane through D, and, since formula (1) holds for D, by corollary to Theorem III, it holds for G. Each conic is cut out by a plane through G, and, since formula (1) holds for G, it holds for each conic. Therefore formula (1) holds for every plane curve on the scroll.

Either double director and G lie on both sheets of the scroll through them, respectively, and G, therefore, intersects either double director twice, once on each sheet, $(2_0, 2_1) = 2$. A plane quartic has a branch on each sheet, at each of the three points where it meets D, D', and G, and it therefore intersects each of these lines twice, once on each sheet, as the formula shows, $(4_1, 2_1) = 2$ and $(4_1, 2_0) = 2$. A plane cubic meets G twice, since it has a branch on each sheet where it crosses G, $(3_1, 2_0) = 2$, but it meets each double director once, since it has a branch on one sheet only, where it crosses either double director, $(3_1, 2_1) = 3 + 2 - 4 = 1$. The plane of a conic passes through G and is tangent to the scroll at two points along G, one on each sheet; these points of tangency are the two points of intersection of the conic and G, $(2_1, 2_0) = 2$, and the conic has a branch on each sheet; one point of tangency lies on the finite segment of G, between D and D', and the other lies on the infinite segment, so that, as we turn the plane about G in one direction, these two points both move toward the intersection of G and D and coincide at this intersection, forming a *pinch point*, when the conic becomes D, i. e. a line on each sheet; if we turn the plane in the other direction, or continue to turn it in the same direction after it cuts out D, the two points of tangency will both move toward D' and will coincide at the pinch point, the intersection of G and D', when the conic becomes D'.

It is easy to see, by the aid of formula (1), how the other plane curves intersect.

4. *Twisted Cubic*, 3_1. — We have seen that $\alpha < \dfrac{a}{2}$ for all twisted curves, and, consequently, every twisted cubic is a 3_1. Also, if δ be the number of points of the curve on D or D', $\delta = a - 2\,\alpha = 1$ for the cubic. The twisted cubic is cut out by a quadric $\left(\nu = \dfrac{a+1}{2}\right)$, and we can make the quadric contain D, since, by formula (2), we have two

points at our disposal in determining the quadric. Every generator then meets the quadric once on the twisted cubic and once on D, and cannot meet it again without lying on it; therefore, the residual consists of D and three generators. Since formula (1) holds for D and the generators, it holds for every twisted cubic on the scroll (Theorem III).

5. *Twisted Quartic* 4_1. — Since $\alpha < \frac{a}{2}$, every twisted quartic is a 4_1; $\delta = a - 2\alpha = 2$; i. e. a plane through D or D' meets the twisted quartic twice on that line. If the curve is a "quartic of the first kind" it may have a double point on D, D', or G, but in any case it has two distinct or consecutive points on one of the double directors, say D, and since we can pass a quadric through a "quartic of the first kind" and any arbitrary point, we may take this arbitrary point on D, and D will then lie on the quadric; if the quartic has no double point on G the residual will then consist of D and G, and if the quartic has a double point on G the residual will consist of D and two generators, since each generator will then meet the quadric once on D and once on the quartic. If the curve is a "quartic of the second kind," it is more convenient to cut it out by a cubic surface, i. e. we take $\nu = 3$; the residual then is of order 8, and by formula (2) we have six points at our disposal in the determination of $S^{(3)}$; since this quartic has no double point, it meets both D and D' in two distinct or consecutive points, and if we put two more points of $S^{(3)}$ on each of these double directors they will both lie on $S^{(3)}$; then G will meet $S^{(3)}$ once on D, once on D', and twice on the quartic, and will, therefore lie on $S^{(3)}$; each generator meets S once on D, once on D', and once on the quartic, and, since we still have two points at our disposal, we can make two generators lie on $S^{(3)}$; the residual will then consist of D, D', G, and two generators. Since formula (1) holds for D, D', G, and the generators, it holds for every twisted quartic on the scroll (Theorem III).

6. *Twisted Curves in General.* — When a is odd we take $\nu = \frac{a+1}{2}$, and the order of the residual is $r = a + 2$. We have seen that $\alpha < \frac{a}{2}$ or $1 \overline{\overline{<}} \alpha \overline{\overline{<}} \frac{a-1}{2}$, and that there is the same number of points, say δ points, on each double director, where $\delta = a - 2\alpha$, i. e. $1 \overline{\overline{<}} \delta \overline{\overline{<}} a - 2$. It has also been shown, p. 25, that we need not consider whether a_α has multiple points on D and D' or not. By formula (2), we have $\frac{a+1}{2}$ points at our disposal, in the determination of $S^{(\nu)}$, and therefore we can

make both D and D' lie on $S^{(\nu)}$ if $\delta + \frac{a+1}{4} \overline{\overline{>}} \frac{a+1}{2} + 1$, i.e. if $\delta \overline{\overline{>}} \frac{a+5}{8}$ or $\alpha \overline{\overline{<}} \frac{3a-5}{8}$. Therefore for $\alpha \overline{\overline{<}} \frac{3a-5}{8}$ the residual can be made to consist of D, D', and a curve of order $r - 4 = a - 2$. When $\alpha > \frac{3a-5}{8}$, at least one point of a_α lies on D, and since we have $\frac{a+1}{2}$ points at our disposal, we can make D lie on $S^{(\nu)}$, and the residual will then consist of D and a curve of order $r - 2 = a$, say a_ρ, where ρ is the number of points of this curve on each generator; now formula (1) holds for D, and if it holds for a_ρ it will hold for a_α (Theorem III), so we need only consider the curve a_ρ; each generator meets $S^{(\nu)}$ in $\nu = \frac{a+1}{2}$ points, once on D, α times on a_α, and ρ times on a_ρ, so that

$$\rho = \frac{a+1}{2} - 1 - \alpha < \frac{a+1}{2} - 1 - \frac{3a-5}{8} \text{ or } \rho < \frac{a+1}{8},$$

i.e. $\rho < \frac{3a-5}{8}$ for $a \overline{\overline{>}} 3$, and a_ρ is therefore a curve like that considered above, that can be cut out by an $S^{(\nu)}$ such that the residual consists of curves of orders less than a.

When a is even, it is convenient to separate the curves into two divisions, according as $\frac{a}{2}$ is odd or even. If $\frac{a}{2}$ is odd we take $\nu = \frac{a}{2}$; then $r = a$, $\alpha < \frac{a}{2}$, and δ must be even since $\delta = a - 2\alpha$; if $\delta \overline{\overline{>}} \frac{a}{2} + 1$, i.e. if $\alpha \overline{\overline{<}} \frac{a-2}{4}$, both D and D' lie on $S^{(\nu)}$ (or can be made to lie on $S^{(\nu)}$), and the residual consists of D, D', and a curve of order $r - 4 = a - 4$; if $\alpha > \frac{a-2}{4}$ the residual is a curve of order a, say an a_ρ, where $\rho = \frac{a}{2} - \alpha < \frac{a}{2} - \frac{a-2}{4}$, or $\rho < \frac{a+2}{4}$; but $\frac{a+2}{4}$ is an integer and ρ is an integer, and therefore $\rho \overline{\overline{<}} \frac{a+2}{4} - 1$, i.e. $\rho \overline{\overline{<}} \frac{a-2}{4}$; therefore, a_ρ is a curve like that just considered, that can be cut out by an $S^{(\nu)}$ such that the residual will consist of curves of orders less than a. If $\frac{a}{2}$ is even we first take $\nu = \frac{a}{2}$, for which $r = a$; δ is even, and if $\delta \overline{\overline{>}} \frac{a}{2} + 2$, i.e. if $\alpha \overline{\overline{<}} \frac{a-4}{4}$, both D and D' lie on $S^{(\nu)}$ (or can be made to lie on

$S^{(\nu)}$), and the residual then consists of D, D', and a curve of order $a - 4$; if $a > \frac{a-4}{4}$, $a \gtreqless \frac{a}{4}$, and when $a > \frac{a}{4}$ the residual is an a_ρ, where $\rho = \frac{a}{2} - a < \frac{a}{2} - \frac{a}{4}$ or $\rho \lesseqgtr \frac{a-4}{4}$, and a_ρ is therefore a curve that can be cut out by an $S^{(\nu)}$ such that the residual will consist of curves of orders less than a; finally, if $a = \frac{a}{4}$ we take $\nu = \frac{a}{2} + 1$; then $r = a + 4$ and $\delta = \frac{a}{2}$; if then we put two more points of $S^{(\nu)}$ on D and two more on D', both of these double directors will lie on $S^{(\nu)}$, and this we can always do, since, by formula (2), we have $a + 2$ points at our disposal in the determination of $S^{(\nu)}$ and $a \gtreqless 4$; then G will meet $S^{(\nu)}$ once on D, once on D', and $2\,a = \frac{a}{2}$ times on a_a, and will therefore lie on $S^{(\nu)}$; each generator will meet $S^{(\nu)}$ once on D, once on D', and $\frac{a}{4}$ times on a_a, and, consequently, if we put $\frac{a}{4}$ more points of $S^{(\nu)}$ on any generator it will lie on $S^{(\nu)}$; now we still have at our disposal $a - 2 \gtreqless 2\left(\frac{a}{4}\right)$ points, since $a \gtreqless 4$, and therefore we can make two generators lie on $S^{(\nu)}$; therefore the residual can be made to consist of D, D', G, two generators, and a curve of order $r - 8 = a - 4$.

Therefore, on this scroll, we may divide all twisted curves into two groups, viz. group (1), those that may be cut out by an $S^{(\nu)}$ such that the residual consists of curves of orders less than a, and group (2), those that may be cut out by an $S^{(\nu)}$ such that the residual is a curve of group (1), with or without D. Now we have seen that formula (1) holds for all plane curves and for all twisted curves of order 3 or 4; it therefore holds for all curves of order 5 of group (1) (Theorem III), and it therefore holds for all curves of order 5 of group (2); it then holds for all curves of order 6 of group (1), and therefore for all curves of order 6 of group (2), and so on. Therefore formula (1) holds for every curve on the scroll.

7. The above proof is also applicable to the *Quartic Scroll, with a two-fold* 2 (+ 2)*-tuple linear director, and with a double generator* $S\,(\overline{1_2\ 1_2},\ 2)$, (*Cayley's Fifth Species*, $S^{V}\,(\overline{1_2\ 1_2},\ 4)$), for this scroll is simply the limiting case of the scroll just considered, where one of the double directors has moved up into coincidence with the other. A plane quartic has a tac-node, where it meets the two-fold director and has a double point on the double generator. A plane cubic, regarded as lying in the

plane, is tangent to the generator in its plane where it meets the two-fold director, but regarded as lying on the scroll, it does not meet the generator there, for they lie on different sheets, and the generator meets the cubic in one point only, where the plane is tangent to the scroll — the formula giving $(1_0, 3_1) = 1$. The system of conics is the same as on the scroll just considered. The two-fold director may be regarded as a 4_2, since it has two lines on each of the two sheets through it and is met twice by each generator. A plane quartic has a branch on each sheet, and therefore meets the two-fold director four times, $(4_1, 4_2) = 8 + 4 - 8 = 4$, while a plane cubic has a branch on one sheet only, and therefore meets this director twice, $(3_1, 4_2) = 6 + 4 - 8 = 2$.

V. Quartic Scroll, with two Double Linear Directors and without a Double Generator, $S(1_2, 1_2, 4)$. (Cayley's First Species, $S(1_2, 1_2, 4)$.)

1. We shall call the double directors D and D'. They do not intersect, and if we pass a plane through either it cuts out two generators. The scroll is similar in many respects to the Quartic Scroll $S(1_2, 1_2, 2)$ already considered, and what was said there in regard to gauch-polygons applies equally well here. But the scroll now under consideration has no double generator, the plane quartic directing curve having only two double points, one on each double director, and this is the only quartic scroll on which the multiple curve is of order less than three.

2. *Proof of Theorem I.* — A plane through D cuts out two generators that meet in a point where the plane meets D', and if we revolve the plane about D, it will cut out, in succession, all the generators of the scroll, two at a time. The plane meets $C^{(a)}$ in a points, of which a definite number, say δ points, lie on D, and therefore there are $a - \delta$ points of $C^{(a)}$ on the two generators in the plane, taken together; for any given curve $C^{(a)}$, the number $a - \delta$ is a constant non-negative integer, say k. Let x and y be the number of points of $C^{(a)}$, respectively, on the two generators lying in a plane through D; then as the plane revolves about D, we always have $x + y = k$, and since x, y, and k are all non-negative integers and k is constant, there is only a finite number of values of x and of y that will satisfy this relation. Let us, for the moment, designate any generator by the number of points of $C^{(a)}$ on it, i. e. the generator x has x points of $C^{(a)}$ on it, etc. To any value of x, say g, there corresponds a certain value of y, say g', such that $g + g' = k$; if then a plane through D cuts out a generator g, it also cuts out a gen-

erator g'. As there is a finite number of pairs of values of x and y, we may arrange them in order of magnitude, calling g the greatest, i. e. we shall say that g is the greatest number of points of $C^{(a)}$ on any generator; correspondingly, g' is the smallest number of points of $C^{(a)}$ on any generator, since $g + g' = k$. Now a plane through D' cuts out two generators, and as we revolve the plane about D' the number of points of $C^{(a)}$ on the two generators in the plane is constant and equal to $a - \delta'$, where δ' is the number of points of $C^{(a)}$ on D'. If then we pass a plane through D' and a generator g', having the least number of points of $C^{(a)}$ on it, the other generator in this plane must have the greatest number g of points of $C^{(a)}$ on it; therefore $g + g' = a - \delta'$, and since $g + g' = a - \delta$, we have $\delta = \delta'$, i. e. $C^{(a)}$ meets each of the double directors, D and D', in the same number of points, δ. If now a plane be passed through a generator g and the director D it will cut out a generator g', and if through this generator g' and D' we pass a plane it will cut out another generator g, so that there are at least two generators g. Through these two generators g, the directors D and D' (which four lines form a gauch-quadrilateral), and an arbitrary point we can pass a quadric; D, D', and the two generators counting for $2 + 2 + 1 + 1 = 6$ lines in the intersection of the quadric and scroll. Each generator meets the quadric in two points, one on D and one on D', and if we take the arbitrary point on any generator, this generator will lie on the quadric, and the remaining intersection of the quadric and scroll will be another generator. Thus by varying this arbitrary point all the generators of the scroll, two at a time, will be successively cut out by a variable quadric that always contains D, D', and the two chosen generators g. This quadric always meets $C^{(a)}$ in $2a$ points, of which 2δ lie on D and D' and $2g$ lie on the two chosen generators g, so that the remaining $2a - 2\delta - 2g$ points lie on the other two generators cut out by the quadric; but $a - \delta = g + g'$ and therefore $2a - 2\delta - 2g = 2g'$. Now there is no generator that has fewer than g' points of $C^{(a)}$ on it and the number of points of $C^{(a)}$ on the two generators together is $2g'$; therefore each must have g' points of $C^{(a)}$ on it. Therefore every generator of the scroll, except the two chosen generators g, has g' points of $C^{(a)}$ on it. In like manner, if we choose two generators g', through which the variable quadric is always to pass, we have the sum of the number of points of $C^{(a)}$ on the other two generators cut out by the quadric always equal to $2a - 2\delta - 2g' = 2g$, and, since no generator has more than g points of $C^{(a)}$ on it, every generator on the scroll, except the two chosen ones, has g points of $C^{(a)}$ on it. Therefore $g = g'$ and

every generator meets $C^{(a)}$ in the same number of points, say α points. Two generators lie in a plane through D; therefore, $\delta = a - 2\,\alpha$, and $\alpha \overline{\overline{<}} \frac{a}{2}$.

2. *Plane Curves.* — D and D' are both 2_1's. There is no system of conics on the scroll, for there is no double generator, and a plane through two generators cuts out D or D'.* A plane through one and only one generator cuts out a plane cubic, a 3_1, that meets each double director once and has no double point, since the section has only three double points which are the points where the generator in the plane meets the cubic, one on each of the double directors, and one where the plane is tangent to the scroll. An arbitrary plane cuts out a plane quartic, a 4_1, having two and only two double points, one on each double director. Every plane curve is, therefore, either the complete intersection of the plane and scroll, or else the residual consists entirely of generators, and consequently, by Theorems II and III, formula (1) holds for every plane curve on the scroll.

3. *Twisted Curves.* — It may be shown in exactly the same way as for the Quartic Scroll, $S\,(1_2, 1_2, 2)$, pp. 33–36, that formula (1) holds for every twisted curve on the scroll. It will be observed that, in the proof referred to, the double generator is shown to be a part of the residual; now, there is no double generator on this scroll, but disregarding the double generator the residual is still composed of curves of orders less than a, and the conclusion follows as before, without change.

4. The proof just employed is also applicable to the *Quartic Scroll with a two-fold* 2 (+ 2)*-tuple linear director and without a double generator*, $S\,(\overline{1_2, 1_2}, 4)$, (*Cayley's Fourth Species*), which is the limiting case of the scroll $S\,(1_2\, 1_2\, 4)$, just considered, where one of the double linear directors has moved up into coincidence with the other.

VI. Quartic Scroll, with a Double Conic and a Double Linear Director meeting it, $S\,(1_2, 2_2, 2)$. (Cayley's Seventh Species, $S\,(1, 2, 2)$.)

1. For convenience, let D represent the double linear director and let K represent the double conic. Any plane through D meets K in one more point, besides the intersection of K and D, and this is a double point on the section by the plane. The plane therefore cuts out D and a

* The section cannot consist of two proper conics. (See p. 25.)

conic having a double point on K, i. e. two lines that meet in this point, which are the two generators in the plane.

2. *Proof of Theorem I.* — The double curve on this scroll is a degenerate twisted cubic, consisting of the double conic K and the double director D. We can pass a quadric through nine arbitrary points, and if we take five of these on K and two on D, distinct from the point of intersection of K and D, K and D will both lie on the quadric and we shall still have two points at our disposal; now every generator meets K and D, and if we take one more point of the quadric on any generator A, it will lie on the quadric; the quadric will then intersect the scroll in K counted twice, D counted twice, and the generator A, and will, therefore, cut out one more generator. Making the quadric always contain K, D, and A, we have one point at our disposal, and by varying this point continuously we make the quadric cut out, in succession, all the generators of the scroll. $C^{(a)}$ meets K, D, and A in a definite number of points, and as it meets every quadric in $2a$ points it meets each generator in the same number of points, say α points. It is evident that A also meets $C^{(a)}$ in α points, for any other generator may be chosen as the one through which the quadric is always to pass, and then A will meet $C^{(a)}$ in the same number of points as the other generators, i. e. in α points. A plane through D cuts out two generators, and there are therefore $a - 2\alpha$ points of a_α on D. K is the complete intersection of its plane and the scroll, and there are therefore a points of a_α on K. The number of points of a_α on D cannot be less than zero, and therefore $\alpha \overline{\overline{<}} \frac{a}{2}$.

3. *Plane Curves.* — The double director D meets every generator once and is therefore a 2_1. The double conic K is met once by each generator and is therefore a 4_1. The section by a plane not through D or K has three double points on the double curve, one on D and two on K. We have seen (p. 25), that the section cannot consist of two proper conics, and we know that a plane through two generators that meet on K, cuts out D, for each generator meets D; therefore, if a plane cuts out a simple conic, it cuts out also two generators that meet in a point on D, for there are no lines on the scroll but the generators, and D and two generators meet only on K or D; conversely, through every point of D pass two generators and their plane cuts out a proper conic; consequently, there is a system of conics that do not meet D, but meet K twice, for clearly the plane cannot meet D again, and the section cannot have a triple point on D unless the plane contains D; each of the two generators in the plane of any conic meets the conic twice, once

in a point where the plane meets K and once where the plane is tangent to the scroll; therefore the section has five double points and the plane is a double tangent plane. The conic and either generator lie on different sheets at the point where they meet K, and, regarding them as lying on the scroll, they do not intersect there. An arbitrary generator meets the plane once, and, since it does not meet either generator in the plane, it meets the conic once, and therefore every conic is a 2_1. Any plane through one and only one generator cuts out a plane cubic, a 3_1, having a double point on K and passing once through each of the points where the generator meets K and D. Any plane that does not contain D, K, or any generator, cuts out a plane quartic, a 4_1, having three double points, two on K and one on D.

The double conic K is the complete intersection of its plane with the scroll, and every plane quartic is the complete intersection of its plane with the scroll, and therefore formula (1) holds for K and for every plane quartic (Theorem II). A plane cubic is cut out by a plane through a single generator, D is cut out by a plane through two generators, and every conic is cut out by a plane through two generators, and therefore formula (1) holds for every plane cubic, for D, and for every conic (Theorem III). Formula (1) holds, therefore, for all plane curves on the scroll.

4. *Twisted Cubic*, 3_1. — Since $a \lesseqgtr \frac{a}{2}$, every twisted cubic is a 3_1. We have seen that there are a points of a_a on K, i. e. there are three points of the twisted cubic on K, and, since we have two points at our disposal in the determination of the quadric that cuts out the twisted cubic, we can take these two points on K and thus make the quadric contain K. The residual, which is of order 5, will then consist of K, which counts for 4, and one generator, and therefore formula (1) holds for every twisted cubic on the scroll (Theorem III).

5. *Twisted Quartics*, 4_2 *and* 4_1. — Since $a \lesseqgtr \frac{a}{2}$, every twisted quartic is either a 4_2 or a 4_1. A 4_2 may be cut out by a quadric; every generator will then meet the quadric twice on the quartic curve 4_2 and cannot meet it again without lying on it; consequently, every generator that has on it a point of the residual must lie on the quadric and form part of the residual, and the residual therefore consists of four generators; therefore formula (1) holds for every 4_2 (Theorem III). For the 4_1, we take $\nu = 3$; then $r = 8$, and we have $19 - 13 = 6$ points at our disposal in the determination of the cubic surface $S^{(3)}$ that cuts out the 4_1. There

are four points of the twisted quartic 4_1 on K, and if we take three more points of $S^{(3)}$ on K, $S^{(3)}$ will contain K; D meets $S^{(3)}$ twice on the curve 4_1, and if we take two more points of $S^{(3)}$ on D, $S^{(3)}$ will contain D; every generator will then meet $S^{(3)}$ once on D, once on K, and once on the curve 4_1, and as we still have one point at our disposal we can make $S^{(3)}$ contain a generator; this generator, D, and K count for 7 in the order of the residual, and therefore $S^{(3)}$ cuts out one more generator. The residual then consists of K, D, and two generators, and therefore formula (1) holds for the twisted quartic 4_1 (Theorem III). Formula (1) holds, therefore, for every twisted quartic.

6. *Twisted Curves in General.* — When a is odd we take $\nu = \frac{a+1}{2}$; then $r = a + 2$, and, by formula (2), we have $\frac{a+1}{2}$ points at our disposal in the determination of $S^{(\nu)}$. If K does not lie on $S^{(\nu)}$, it meets $S^{(\nu)}$ in $2\left(\frac{a+1}{2}\right) = a + 1$ points; but we have seen that there are a points of a_a on K, and consequently, if we take two more points of $S^{(\nu)}$ on K, $S^{(\nu)}$ will contain K; this we can always do, since the number of points at our disposal is $\frac{a+1}{2} \geqq 2$ for $a \geqq 3$. The residual will then consist of K and a curve of order $r - 4 = a - 2$.

When a is even, we distinguish two kinds of curves according as $\frac{a}{2}$ is odd or even. If $\frac{a}{2}$ is odd we take $\nu = \frac{a}{2}$; then $r = a$, and if δ be the number of points of a_α on D, we have seen that $\delta = a - 2\alpha$: now, if $\delta \geqq \frac{a}{2} + 1$, i.e. if $\alpha \leqq \frac{a-2}{4}$, D meets $S^{(\nu)}$ in at least $\frac{a}{2} + 1 = \nu + 1$ points,* and therefore lies on $S^{(\nu)}$, so that the residual consists of D and a curve of order $r - 2 = a - 2$; if $\alpha > \frac{a-2}{4}$, the residual either breaks up into curves of orders less than a, or else it is a curve of order a, say an a_ρ, where $\rho = \frac{a}{2} - \alpha$, since each generator meets $S^{(\nu)}$ in $\nu = \frac{a}{2}$ points, of which α lie on a_α and ρ on a_ρ; then, since $\alpha > \frac{a-2}{4}$, $\rho < \frac{a+2}{4}$; but ρ is an integer and $\frac{a+2}{4}$ is an integer, so that $\rho \leqq \frac{a+2}{4} - 1$, i.e. $\rho \leqq \frac{a-2}{4}$, and a_ρ is therefore one of the curves

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* Or $S^{(\nu)}$ can be made to pass through $\nu + 1$ points of D. (See p. 25.)

just considered, that can be cut out by such an $S^{(\nu)}$ that the residual will consist of D and a curve of order $a-2$. If $\frac{a}{2}$ is even and $\nu = \frac{a}{2}$, the residual is of order a; then δ must be even, being equal to $a - 2\alpha$, and, if $\delta \overline{\gtrless} \frac{a}{2} + 2$, i.e. if $\alpha \overline{\lessgtr} \frac{a-4}{4}$, D lies on $S^{(\nu)}$, and the residual consists of D and a curve of order $a-2$. If $\alpha > \frac{a-4}{4}$, then $\alpha \overline{\gtrless} \frac{a}{4}$. When $\alpha > \frac{a}{4}$ the residual either breaks up into curves of orders less than a, or else it is a curve of order a, say an a_ρ, where $\rho = \nu - \alpha < \frac{a}{4}$, i.e. $\rho \overline{\lessgtr} \frac{a-4}{4}$, and consequently a_ρ is a curve like that just considered, that can be cut out by an $S^{(\nu)}$ such that the residual will consist of D and a curve of order $a-2$. Finally, when $\alpha = \frac{a}{4}$, we take $\nu = \frac{a}{2} + 1$; then $r = a + 4$, and, by formula (2), we have $a + 2$ points at our disposal in the determination of $S^{(\nu)}$. If K does not lie on $S^{(\nu)}$, it meets $S^{(\nu)}$ in $a + 2$ points; now K has a points of a_α on it, and if we make $S^{(\nu)}$ pass through three more points of K, not on a_α, $S^{(\nu)}$ will contain K; this we can always do and still have at least three more points at our disposal, since $a + 2 \overline{\gtrless} 6$ for $a \overline{\gtrless} 4$. Since $\alpha = \frac{a}{4}$, $\delta = \frac{a}{2}$, and if we make $S^{(\nu)}$ pass through two more points of D, not on a_α, $S^{(\nu)}$ will cut out D. The residual will then consist of K, D, and a curve of order $r - 4 - 2 = a - 2$.

The twisted curves on this scroll can therefore be divided into two groups, viz., group (1), those curves of order a, each of which can be cut out by such an $S^{(\nu)}$ that the residual will consist of curves of orders less than a, and group (2), those curves of order a, each of which can be cut out by such an $S^{(\nu)}$ that the residual will be a curve of order a and of group (1). Therefore, by the same reasoning as that employed for Quartic Scroll $S(1_2, 1_2, 2)$, p. 36, Formula (1) holds for all curves on the scroll.

VII. Quartic Scroll, with a Double Twisted Cubic met twice by each Generator and with a Simple Linear Director, $S(3_2{}^2, 1)$. (Cayley's Eighth Species, $S(1, 3^2)$.)

1. Let Q represent the twisted cubic, which is the double curve on the scroll. Through each point of Q pass two generators; the plane of these two generators contains the linear director, since each generator

meets the linear director once, and therefore this plane cuts out also a third generator, i.e. any plane through the linear director meets Q in three points, say L, M, and N, and cuts out the three generators $L\,M$, $M\,N$, and $N\,L$.

2. *Proof of Theorem I.* — We can make a quadric pass through Q by making it pass through seven points of Q; and since Q is a double cubic it counts for six in the order of the complete intersection of the quadric and scroll; if the eighth point for the determination of the quadric be taken on any generator A, the quadric will contain A, since each generator meets Q twice; the remaining intersection will be any generator on which we choose to take the ninth point for the determination of the quadric, and if we keep the first eight points fixed and vary the ninth point continuously, the quadric will cut out in succession the different generators of the scroll. A fixed number of points of $C^{(a)}$ lie on Q and the chosen generator A, and therefore every generator contains the same number of points of $C^{(a)}$, say α points. Any generator, other than A, can be chosen, through which the quadric is always to pass, and therefore there are α points of $C^{(a)}$ on A. Since the quadric meets a_α in $2\,a$ points, there are $2\,a - 2\,\alpha = 2\,(a - \alpha)$ points of a_α on Q. Three generators lie in a plane through the linear director; therefore $\alpha \leqq \frac{a}{3}$, and there are $a - 3\,\alpha$ points of a_α on the linear director.

3. *Plane Curves.* — Since the section by a plane cannot consist of two proper conics (p. 25), a plane through a proper conic would either cut out two generators or the simple director and one generator; but we have seen that a plane through two generators or through the simple linear director cuts out three generators and the linear director; therefore there can be no proper conic on the scroll.

A plane through one, and only one, generator cuts out a plane cubic, a 3_1, having a double point on Q and passing once through each of the two points where the generator meets Q; the generator meets the plane cubic in one other point where the plane is tangent to the scroll. An arbitrary plane cuts out a plane quartic, a 4_1, having three double points on Q, and since any plane quartic is the complete intersection of its plane with the scroll, formula (1) holds for it (Theorem II). The simple linear director, a 1_1, is cut out by a plane through three generators, and every plane cubic is cut out by a plane through one generator, and therefore formula (1) holds for the simple linear director and for every plane cubic (Theorem III). Therefore formula (1) holds for all plane curves on the scroll.

The double cubic Q, although not a plane curve, will be considered here. We have seen that it is cut out by a quadric through two generators, and therefore formula (1) holds for it (Theorem III). It is met twice by every generator, and is, therefore, a 6_2. A plane quartic has a branch on each sheet at each of the three points where it meets Q, and the number of its intersections with Q is 6, $(6_2, 4_1) = 6 + 8 - 8 = 6$. A plane cubic meets Q four times, twice at the double point of the plane cubic and once at each of the other two points where the plane meets Q, $(6_2, 3_1) = 6 + 6 - 8 = 4$. The linear director does not meet Q, $(6_2, 1_1) = 6 + 2 - 8 = 0$.

4. *Twisted Cubic*, 3_1.—Since $\alpha \overline{\gtrless} \frac{a}{3}$, every twisted cubic is a 3_1. We take $\nu = 3$; then $r = 9$, and we have $19 - 10 = 9$ points at our disposal in the determination of $S^{(3)}$ that cuts out the twisted cubic. The number of points of the twisted cubic on Q is $2(a - \alpha) = 4$, and if we take 6 more points of $S^{(3)}$ on Q, $S^{(3)}$ will contain Q; this leaves $9 - 6 = 3$ points at our disposal, and, since each generator now meets $S^{(3)}$ twice on Q and once on the twisted cubic, we can take one more point of $S^{(3)}$ on each of three generators and $S^{(3)}$ will then contain those three generators; the residual will then consist of Q and three generators, and therefore formula (1) holds for every twisted cubic (Theorem III). Since three generators lie in a plane through the linear director, a twisted cubic does not meet the linear director, $(3_1, 1_1) = 3 + 1 - 4 = 0$.

5. *Twisted Quartic* 4_1.—Since $\alpha \overline{\gtrless} \frac{a}{3}$, every twisted quartic is a 4_1. We take $\nu = 3$; then $r = 8$, and the number of points at our disposal in the determination of $S^{(3)}$ is $19 - 13 = 6$. There are $2(a - \alpha) = 6$ points of the twisted quartic on Q, and if we take four more points of $S^{(3)}$ on Q, $S^{(3)}$ will contain Q. Each generator will then meet $S^{(3)}$ twice on Q, and once on the twisted quartic, and, since we still have two points at our disposal, we can make $S^{(3)}$ cut out two generators. The residual will then consist of Q and two generators, and therefore formula (1) holds for every twisted quartic.

6. *Twisted Curves in General.*—When a is odd we take $\nu = \frac{a+3}{2}$; then $r = a + 6$, and by formula (2) we have $\frac{3a+9}{2}$ points at our disposal in the determination of $S^{(\nu)}$. If δ be the number of points of a_α on Q, $\delta = 2(a - \alpha) \overline{\gtrless} \frac{4a}{3}$, since $\alpha \overline{\gtrless} \frac{a}{3}$. That $S^{(\nu)}$ may contain Q, it must

pass through $3\nu + 1 = \frac{3a + 11}{2}$ points of Q, and therefore, if we take $\frac{3a + 11}{2} - \delta \overline{\gtrless} \frac{a + 33}{6}$ of the points at our disposal on Q, $S^{(\nu)}$ will contain Q; if λ be the number of points left at our disposal, after making $S^{(\nu)}$ contain Q, $\lambda \overline{\gtrless} \frac{3a + 9}{2} - \frac{a + 33}{6}$, i. e. $\lambda \overline{>} \frac{4a}{3} - 1$. Now each generator meets $S^{(\nu)}$ twice on Q and α times on a_α, i. e. at least three times since $\alpha \overline{\gtrless} 1$; if, then, we make $S^{(\nu)}$ pass through $\frac{a + 3}{2} + 1 - 3 = \frac{a - 1}{2}$ other points on any generator, that generator will lie on $S^{(\nu)}$. We can, therefore, make at least two generators lie on $S^{(\nu)}$, since $\frac{4a}{3} - 1 > 2\left(\frac{a - 1}{2}\right)$, and the residual will then consist of Q, two generators, and a curve of order $r - 6 - 2 = a - 2$.

When a is even we take $\nu = \frac{a}{2} + 1$; then $r = a + 4$, and, by formula (2), we have $a + 2$ points at our disposal in the determination of $S^{(\nu)}$. The number of points of a_α on Q is $\delta = 2(a - \alpha) \overline{\gtrless} \frac{4a}{3}$. In order for $S^{(\nu)}$ to contain Q, it must pass through $3\nu + 1 = \frac{3a + 8}{2}$ points of Q, and therefore in addition to the δ points we must make $S^{(\nu)}$ pass through $\frac{3a + 8}{2} - \delta \overline{\lessgtr} \frac{a + 24}{6}$ other points of Q; this we can always do, since the number of points at our disposal is $a + 2 > \frac{a + 24}{6}$ for $a \overline{\gtrless} 4$. The residual will then consist of Q and a curve of order $r - 6 = a - 2$.

We have shown, then, that every twisted curve of order a can be cut out by an $S^{(\nu)}$ such that the residual is composed of curves of orders less than a; we have also shown that formula (1) holds for every plane curve and for every twisted curve of order 3 or 4; it holds, therefore, for every twisted curve of order 5, and therefore for every twisted curve of order 6, and so on (Theorem III); therefore formula (1) holds for every curve on the scroll.

VIII. Quartic Scroll, with a Double Twisted Cubic met Twice by each Generator, $S(3_2^2, 2)$. (Cayley's Tenth Species, $S(3^2)$.)

1. Let Q be the double twisted cubic. Through every point of Q pass two generators. The scroll differs from the Quartic Scroll $S(3_2^2, 1)$

in not having a simple linear director, in consequence of which a plane through two generators cuts out a proper conic.

2. *Proof of Theorem I.* — By passing a quadric surface through Q and any chosen generator, Theorem I is proved in exactly the same way as it is for the Quartic Scroll $S(3_2^2, 1)$, p. 44., and if α be the number of points of $C^{(a)}$ on each generator, we see, as before, that the number of points of a_α on Q is $2(a-\alpha)$. Since two generators lie in a plane, $\alpha \overline{\overline{<}} \frac{a}{2}$.

3. *Plane Curves.* — Since there are no lines on the scroll except the generators, a plane through two generators cuts out a proper conic, and since the section has three double points on Q, the conic passes through each of the two points in which the generators meet Q, different from their point of intersection. Each conic is a 2_1, and regarding the conic and generators as lying on the scroll, the conic is met once only by each generator in its plane, since at the point where the conic and generator cross Q they lie on different sheets. The two points where the two generators meet the conic, not on Q, are points of tangency of the plane, and therefore through every point of Q there is a double tangent plane to the scroll. By Theorem III, formula (1) holds for every conic. There is no 1_1 on the scroll, and the other plane curves, the cubic, 3_1, and the quartic, 4_1, are the same as those of the same order on the Quartic Scroll $S(3_2^2, 1)$ and therefore formula (1) holds for all curves on the scroll. Since Q is a double twisted cubic met twice by each generator, it is a 6_2, and since it is cut out by a quadric through two generators, formula (1) holds for it (Theorem III). We have seen that Q meets each conic twice, and the formula gives

$$(6_2, 2_1) = 6 + 4 - 8 = 2.$$

4. *Twisted Curves.* — It is proved in exactly the same way as for the Quartic Scroll $S(3_2^2, 1)$ that formula (1) holds for every twisted curve on the scroll; therefore, it holds for every curve on the scroll.

IX. Quartic Developable.

1. This surface is formed by the tangents to a twisted cubic, E; E is then a double curve on the surface, and from one point of view, this surface is the limiting case of the Quartic Scroll $S(3_2^2, 1)$ where the two points in which any generator meets the twisted cubic have become consecutive; the twisted cubic then becomes the "edge of regression" and the three double points of the section by a plane become cusps.

2. *Proof of Theorem I.* — By passing a quadric through E, which is the cuspidal edge of the developable, and any chosen generator, Theorem I is proved in exactly the same way as it is for the Quartic Scroll $S(3_2^2, 1)$, p. 44, and if a be the number of points of $C^{(a)}$ on each generator, E has $2(a - \alpha)$ points of a_α on it. Since E is cut out by a quadric through two generators, formula (1) holds for it (Theorem III). Being a double twisted cubic met twice by each generator, E is a 6_2 and formula (1) gives, for the number of intersections of E with a_α,

$$(6_2, a_\alpha) = 6\alpha + 2a - 8\alpha = 2(a - \alpha).$$

3. *Plane Curves.* — A "plane of the system," i. e. an osculating plane of E, cuts out two consecutive generators and a proper conic.* This conic, which is tangent to E,† can never break up, for there are no lines on the surface except the generators, and a plane cannot contain more than two generators (which must, moreover, be consecutive), since it cannot meet E in more than three points. Each conic is a 2_1, and there is a conic through every point of E.

A plane through one and only one generator cuts out a plane cubic, a 3_1, that has a cusp at the point not on the generator, where the plane meets E, and has the generator for its real inflectional tangent at the point where the generator meets E; for, since the two consecutive points in which the generator meets E must be double points of the section of a plane through the generator, the plane cubic must pass through each of these points, i. e. it meets the generator in at least two points there; but the generator at this point crosses from one sheet to the other, say from the upper to the lower, while the plane cubic crosses from the lower to the upper; therefore they cross each other and intersect in an odd number of points, and consequently they intersect in three points, i. e. the generator is the real inflectional tangent.

Every plane quartic has three cusps, one at each of the three points where its plane meets E, and since it is the complete intersection of its plane with the developable, formula (1) holds for it (Theorem II).

Every conic is cut out by a plane through two generators and every plane cubic is cut out by a plane through one generator, and therefore formula (1) holds for every conic and for every plane cubic (Theorem III). Formula (1) holds, therefore, for every plane curve on the developable.

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* Salmon's Geom. of Three Dimensions, § 339.

† V. Jamet, C. R., 1885, Vol. 100, pp. 1332–35.

4. *Twisted Curves.* — It may be shown in exactly the same way as for the Quartic Scroll $S(3_2^2, 1)$, that formula (1) holds for every twisted curve on the developable.

Formula (1) holds, therefore, for every curve on the developable.

X. Quartic Cones.

1. Using the plane quartic curves as a base, we may say that there are ten different species of quartic cones, corresponding to the ten species of plane quartic curves.* But for our present purpose we need not distinguish between double edges and cuspidal edges, and it will be convenient to divide the cones into five groups, viz., (I) cones having a triple edge, (II) cones having three edges double or cuspidal, (III) cones having two edges double or cuspidal, (IV) cones with one double or cuspidal edge, and (V) non-singular cones, i. e. cones with no multiple edges.†

A curve $C^{(a)}$, lying on a cone, has a k-tuple point at the vertex, where $0 \gtreqless k$, and any plane through the vertex meets $C^{(a)}$ in k points there.

2. *Theorem I.* — Every edge of a quartic cone meets $C^{(a)}$ in the same number of points, say α points (in addition to the k points at the vertex); the number of points of $C^{(a)}$ on a double edge is 2α, and the number of points of $C^{(a)}$ on a triple edge is 3α.

Proof. — Considering group (I), if we pass a plane through the triple edge and revolve it about this triple edge, it will cut out, in succession, all the edges of the cone; the plane meets $C^{(a)}$ in k points at the vertex and in a fixed number of points, say τ points, on the triple edge, and, as it meets $C^{(a)}$ altogether in a points, the same number of points, say α points, lie on each edge of the cone. An arbitrary plane through the vertex meets the cone in four edges, and therefore

$$4\alpha + k = a, \qquad \text{i. e. } 4\alpha = a - k.$$

Taking the plane through the triple line, we have

$$\alpha + \tau = a - k = 4\alpha, \qquad \text{i. e. } \tau = 3\alpha.$$

Consider now group (II), and pass a quadric cone through the three double or cuspidal edges and any chosen edge A of the quartic cone; these count for seven edges in the intersection of the two cones, and

* Salmon's Higher Plane Curves, § 243.

† When not qualified by the words *double, cuspidal, triple, multiple*, etc., the word *edge* will always mean a *simple edge* of the cone.

they must have one more edge in common; if, then, we vary continuously the fifth arbitrary edge that determines the quadric cone, this cone will always pass through the three double or cuspidal edges and the edge A of the quartic cone, and will cut out all the edges of the quartic cone one at a time. Every quadric cone meets $C^{(a)}$ in $2a$ points, of which a definite number lie on the three double or cuspidal edges and the edge A, and therefore the same number of points of $C^{(a)}$, say α points, lie on each edge of the quartic cone; it is evident that, if any other edge be chosen through which the quadric cone is always to pass, the edge A will have α points of $C^{(a)}$ on it. If we pass an arbitrary plane through any of the double or cuspidal edges, it will also cut out two edges of the quartic cone, and, if δ be the number of points of $C^{(a)}$ on this double or cuspidal edge, we have

$$\delta + 2\alpha = a - k = 4\alpha, \qquad \text{i.e. } \delta = 2\alpha,$$

since an arbitrary plane through the vertex cuts out four edges, giving $4\alpha = a - k$.

To prove the theorem for group (III), we may employ a method analogous to that used for the Quartic Scroll $S(1_2, 1_2, 4)$, p. 37; corresponding to the planes there, through the double directors, we should use here the planes through the double or cuspidal edges, and instead of the quadric used there we should now employ a quadric cone.

We shall not consider this proof in detail, but shall now give a proof of the theorem for groups (IV) and (V), — a proof which holds for the other three groups as well, and therefore for all quartic cones.

If p is the number of points of $C^{(a)}$ on any edge of the cone, it is evident that $0 \overline{\overline{<}} p \overline{\overline{<}} a - 1$, and p can have, at most, a different values. For convenience, we shall say that all the edges for which p has the same value belong to the same set; and if there is an infinite number of edges in a set, we shall call it an infinite set, or, if there is a finite number, a finite set. There are, at most, a different sets, and, since a is finite, at least one of these must be an infinite set. Let us suppose, first, that there is only one infinite set, and let α be the value of p for this infinite set; we can then pass a plane through one of these α-edges (i. e. an edge having α points of $C^{(a)}$ on it) and turn it about so that it shall not contain any edge of any finite set; this plane will then cut out four α-edges, and as it meets $C^{(a)}$ in a points, of which k lie at the vertex, we have

$$4\alpha + k = a, \qquad \text{i.e. } a - k = 4\alpha.$$

Now we can pass a plane through any edge of any of the finite sets and

turn it about so that it will not contain any other edge of any finite set, and this plane will then cut out three α-edges in addition to the chosen edge; if β is the number of points of $C^{(a)}$ on the chosen edge, we have

$$\beta + 3\alpha = a - k = 4\alpha, \qquad \text{i. e. } \beta = \alpha.$$

Therefore every edge of the cone has α points of $C^{(a)}$ on it. If the cone has a double or cuspidal edge, an arbitrary plane through it will cut out two α-edges, and if δ is the number of points of $C^{(a)}$ on the double or cuspidal edge

$$\delta + 2\alpha = a - k = 4\alpha, \qquad \text{i. e. } \delta = 2\alpha.$$

If the cone has a triple edge, having τ points of $C^{(a)}$ on it, an arbitrary plane through this triple edge will cut out one α-edge, and we have

$$\tau + \alpha = a - k = 4\alpha, \qquad \text{i. e. } \tau = 3\alpha.$$

Therefore, the theorem holds when there is only one infinite set. Suppose now that any number of the a sets are infinite, and let α be the least value of p belonging to any of these infinite sets. Pass a cubic cone through nine of these α-edges; then, since the cubic cone meets $C^{(a)}$ in $3a$ points, of which $3k$ lie at the vertex and 9α on the nine chosen edges, the remaining $3a - 3k - 9\alpha$ points lie on the three other edges in which the cubic and quartic cones intersect, and at least one of these three edges must have as many as $a - k - 3\alpha$ points of $C^{(a)}$ on it. Keeping seven of the α-edges fixed, we can vary the other two in such a way that the cubic cone, determined each time by the nine α-edges, will have for its remaining intersection with the quartic cone three edges different from those of any other such cone previously determined; since there is an infinite number of α-edges, we get, in this way, an infinite number of such cubic cones, and therefore an infinite number of edges each having as many as $a - k - 3\alpha$ points of $C^{(a)}$ on it; having an infinite number of such edges, we can so choose two of them that their plane will not pass through any edge of any finite set, because there is a finite number of edges in all the finite sets taken together; besides the chosen edges this plane will then cut out two edges belonging to the infinite sets. Now the number of points of $C^{(a)}$ on the two chosen edges taken together is equal to or greater than $2a - 2k - 6\alpha$, and if β and γ be the number of points of $C^{(a)}$, respectively, on the other two edges in the plane we must have

$$2a - 2k - 6\alpha + \beta + \gamma \overline{\overline{<}} a - k,$$

and, since neither β nor γ can be less than α,

$$2a - 2k - 6\alpha + 2\alpha \overline{\overline{<}} a - k,$$

i. e. $$a - k \overline{\overline{<}} 4\,\alpha.$$

If, now, we pass a plane through any edge of any infinite set and turn it about so that it will not pass through any edge of any finite set, it will cut out three other edges of the infinite sets. Let p_1, p_2, p_3, and p_4 be the number of points of $C^{(a)}$, respectively, on the four edges in this plane; we have then

$$p_1 + p_2 + p_3 + p_4 = a - k \overline{\overline{<}} 4\,\alpha,$$

and, since neither p_1, p_2, p_3, nor p_4 can be less than α, each must be equal to α and $a - k = 4\,\alpha$. Therefore, every edge of every infinite set meets $C^{(a)}$ in α points, i. e. there is only one infinitive set, and we have proved that the theorem holds in this case.

3. On the cones, a curve $C^{(a)}$ is, as before, designated by the symbol a_α, but α now means the number of points, other than those at the vertex, in which an arbitrary edge of the cone meets the curve $C^{(a)}$. We shall now show that formula (1), $(a_\alpha, b_\beta) = a\,\beta + b\,\alpha - 4\,\alpha\,\beta$, gives, for the quartic cones, the number of intersections of the two curves, a_α and b_β, exclusive of the number of their intersections at the vertex of the cone.

We have seen that $a - k = 4\,\alpha$, i. e. $k = a - 4\,\alpha$, where k is the number of branches of a_α through the vertex, i. e. a_α has an $(a - 4\,\alpha)$-tuple point at the vertex. Let a_α be the complete intersection of $S^{(\nu)}$ and the quartic cone, and let b_β be an arbitrary curve on the cone; the total number of intersections of a_α and b_β is the number of intersections of $S^{(\nu)}$ and b_β, which is $b\,\nu$, and, since $a = 4\,\nu$, $b\,\nu = \frac{a\,b}{4}$; now, at the vertex, $S^{(\nu)}$ has a point of multiplicity $\frac{a - 4\,\alpha}{4}$ (since a_α is the complete intersection of $S^{(\nu)}$ and the cone and has an $(a - 4\,\alpha)$-point at the vertex), and b_β has a $(b - 4\,\beta)$-tuple point, so that b_β meets $S^{(\nu)}$ in

$$\left(\frac{a - 4\,\alpha}{4}\right)(b - 4\,\beta) = \frac{a\,b}{4} - (a\,\beta + b\,\alpha - 4\,\alpha\,\beta)$$

points at the vertex; since the total number of intersections of b_β and $S^{(\nu)}$ is $\frac{a\,b}{4}$, the number of their intersections exclusive of those at the vertex, i. e. the number of intersections of b_β and a_α exclusive of those at the vertex, is $\frac{a\,b}{4} - \frac{a\,b}{4} + (a\,\beta + b\,\alpha - 4\,\alpha\,\beta) = a\,\beta + b\,\alpha - 4\,\alpha\,\beta$, which is the number given by formula (1).

Since the formula holds when a_α is the complete intersection of the cone and $S^{(\nu)}$, by Theorem III, it holds when a_α is the partial intersec-

tion of the cone and $S^{(\nu)}$, provided we can always cut out a_a by an $S^{(\nu)}$ such that the residual is of order less than a or breaks up into components, each of which is of order less than a; for we know that it holds for the number of intersections of any edge, a 1_0, with an arbitrary curve b_β, giving $(1_0, b_\beta) = \beta$. Each edge is a 1_0, each double or cuspidal edge is a 2_0, and each triple edge is a 3_0, since the edges and multiple edges meet only at the vertex. Every multiple edge can be cut out by a plane such that the residual will consist entirely of generators, and therefore formula (1) holds for every multiple edge (Theorem III). Since the plane quartic cannot break up without the cone breaking up (unless it consists entirely of edges or multiple edges), the only plane curve, besides the edges and multiple edges, that can lie on the cone is a plane quartic which is the complete intersection of its plane with the cone, and therefore formula (1) holds for every plane curve.

4. *Twisted Curves.* — There is no cubic curve on a quartic cone, since $1 \gtreqless a$ and $4\alpha \gtreqless a$, and, therefore, $4 \gtreqless a$.

Every twisted quartic is a 4_1, since $\alpha \gtreqless \frac{a}{4}$, and, since $k = a - 4\alpha = 0$, it does not go through the vertex. Any twisted quartic can be cut out by a cubic monoid,* for we can pass the monoid through $19 - 4 = 15$ arbitrary points, and if we take thirteen of these on the quartic curve, the monoid will contain it. The node of the monoid is taken at the vertex of the cone; each edge of the cone then meets the cubic monoid twice at the vertex and once on the quartic curve, and cannot meet it again without lying on it; therefore the monoid cannot meet the cone in any other curve, and the residual consists entirely of edges or multiple edges of the cone.

Every twisted quintic is a 5_1, and has one branch through the vertex, $k = 5 - 4 = 1$; it can be cut out by a cubic monoid which can be passed through 15 arbitrary points; for the quintic meets the monoid twice at the vertex, and if we pass the monoid through 14 other points of the quintic, it will contain the quintic. Every edge of the cone meets the monoid twice at the vertex and once on the quintic curve, and therefore the residual consists entirely of edges or multiple edges of the cone.

Every twisted sextic is a 6_1, and has two branches through the vertex, since $k = 6 - 4 = 2$; it can be cut out by a cubic monoid whose node is at the vertex of the cone; for the sextic meets the monoid four times

* A *monoid* of order m is a surface of order m having an $(m-1)$-tuple point. (Cayley.)

at the vertex, and if we pass the monoid through 15 other points of the sextic it will contain the sextic. The residual will then consist entirely of edges or multiple edges of the cone.

In the same way it may be shown that all curves of order 7, and all curves of orders 8, 9, and 10 for which $\alpha = 1$, can be cut out by a quartic monoid such that the residual will consist of edges or multiple edges of the cone.

When $\alpha \gtreqless 2$ (for which $a \gtreqless 8$), or when $a \gtreqless 11$, i. e. for all curves not yet considered, we must take $\nu \gtreqless 5$, where ν is the order of the surface of lowest order that cuts out a_α such that the residual consists of edges or multiple edges of the cone. We shall now show that such a surface can be found for any a_α, and the value of ν given in terms of a and α. Since the residual is to consist entirely of edges or multiple edges of the cone, an arbitrary edge must meet the required surface in $\nu - a$ points at the vertex, i. e. the surface must have a $(\nu - a)$-tuple point at the vertex of the cone. Let $M^{(\nu)}_{\nu - a}$ be the required surface. When $\nu > 4$ we must take care that $M^{(\nu)}_{\nu - a}$ does not break up into the quartic cone and a surface which must be an $M^{(\nu - 4)}_{\nu - a - 4}$, i. e. a surface which has a $(\nu - a - 4)$-tuple point at the vertex; $M^{(\nu - 4)}_{\nu - a - 4}$ can pass through only

$$\tfrac{1}{6}\left[(\nu - 3)(\nu - 2)(\nu - 1) - (\nu - a - 4)(\nu - a - 3)(\nu - a - 2)\right] - 1$$

arbitrary points, different from the vertex, and consequently if we make $M^{(\nu)}_{\nu - a}$ pass through

$$\text{(A)} \quad \tfrac{1}{6}\left[(\nu - 3)(\nu - 2)(\nu - 1) - (\nu - a - 4)(\nu - a - 3)(\nu - a - 2)\right]$$

arbitrary points, not on the quartic cone, it cannot have the quartic cone as a component; the number of arbitrary points remaining, to determine $M^{(\nu)}_{\nu - a}$, must be great enough to make it contain a_α, which has $a - 4\alpha$ branches through the vertex; consequently we have

$$\begin{aligned}(3)\ \ldots\quad a\nu + 1 - (a - 4\alpha)(\nu - a) \leqq \tfrac{1}{6}\big[&(\nu + 1)(\nu + 2)(\nu + 3) \\ &- (\nu - a)(\nu - a + 1)(\nu - a + 2) - (\nu - 3)(\nu - 2)(\nu - 1) \\ &+ (\nu - a + 4)(\nu - a - 3)(\nu - a - 2)\big] - 1,\end{aligned}$$

from which we obtain the relation

$$1 + \alpha a + 4a\nu - 4a^2 \leqq 4a\nu - 2a^2 + 4\nu - 4a - 3,$$

i. e.

$$(4)\ \ldots \qquad \nu = \frac{a(a - 2\alpha + 4) + 4}{4},$$

or the next greater integer. When $\nu = 3$ or 4 we saw that $a = 1$, so that the expression (A) that enters into eq. (3) vanishes for $\nu = 3$, as it should, and is equal to unity for $\nu = 4$; therefore eq. (4) gives the correct value of ν for all twisted curves on the cone. If then we take the value of ν given by eq. (4), any twisted curve a_a can be cut out by an $M^{(\nu)}_{\nu-a}$ such that the residual will consist entirely of edges or multiple edges of the cone, and therefore formula (1) holds for all twisted curves on the quartic cones. In determining the above value of ν, no account was taken of the actual multiple points, not at the vertex, that a_a may have. We have seen (p. 24) that an m-tuple point reduces by $m - 1$ the number of points of a_a through which it is necessary to make $M^{(\nu)}_{\nu-a}$ pass in order for it to contain a_a, if this m-tuple point be taken as one of them; therefore, if $a\ (a - 2\,a + 4) + 4 \equiv 1$ (mod. 4) and a_a has a double point not at the vertex, the value of ν may be taken one less than that given by eq. (4); if $a\ (a - 2\,a + 4) + 4 \equiv 2$ (mod. 4) and a_a has two double points or one triple point, not at the vertex, the value of ν from eq. (4) is reduced by unity, and so on. If a_a has four double points, or two triple points, or two double points and a triple point, or a double point and a 4-tuple point, or one 5-tuple, not at the vertex, then the value of ν is always one less than that given by eq. (4).

We have shown, then, that formula (1) gives the number of intersections, aside from those at the vertex, of any two curves on any quartic cone. It is to be observed that any branch of a_a through the vertex has an edge of the cone as its tangent at that point and that one of the two consecutive points, in which the edge meets the branch there, is one of the a points of a_a that lie on this edge; if a double or cuspidal edge is tangent to a branch of a_a at the vertex, then two of the $2\,a$ points of a_a that lie on it are consecutive to the vertex; and if a triple edge is tangent to a branch of a_a at the vertex, then three of the $3\,a$ points of a_a that lie on it are consecutive to the vertex. If, therefore, a_a and b_β each have a branch through the vertex tangent to the same edge, i. e. a branch of a_a tangent to a branch of b_β at the vertex, then one of these two intersections of the curves at this point is included in the number of intersections given by formula (1). In like manner, if a_a and b_β each have a branch through the vertex, and these branches have there a common inflectional or cuspidal tangent or have any peculiar relation to one another, the excess of the number of intersections that these branches have there over the number of intersections that two arbitrary branches would have there is included in the number of intersections given by formula (1).

5. We shall now consider the twisted quartics more in detail. Every twisted quartic is a 4_1, and, since it has at least two apparent double points, the cone on which it lies must have at least two double or cuspidal edges, i. e. no twisted quartic can lie on the cones of groups (IV) and (V); moreover, the cubic monoid, which cuts out the twisted quartic, has six * lines on it through the vertex, and these six lines must count for eight, the order of the residual intersection of the cone and monoid, and therefore the cone must have, at least, two double or cuspidal edges with which two of the six lines coincide. Through a "quartic of the first kind" can be passed an infinity of quadrics, i. e. we can pass a quadric through a "quartic of the first kind" and any arbitrary point; let this quadric be passed through the vertex. The "quartic of the first kind" has two apparent double points, and the two double edges, of the cone, on which they lie, meet the quadric twice on the curve and once at the vertex, and therefore lie entirely on it; these double edges are, therefore, the two generators of opposite systems, of the quadric, through the vertex. The cubic monoid, in this case, breaks up into the quadric and a plane through the vertex. The "quartic of the first kind" may have an actual double point or cusp, in which case the cone has an additional double or cuspidal edge that meets the quadric only once at this double point or cusp and once at the vertex, and therefore does not lie on it. The cone may have a cuspidal edge due to an apparent cusp on the quartic curve, i. e. if a tangent to the curve passes through the vertex, the curve when viewed from the vertex appears to have a cusp on this tangent, which is therefore a cuspidal edge of the cone (the apparent cusp replaces one of the apparent double points and the cuspidal edge is one of the generators of the quadric). If two tangents to the quartic curve pass through the vertex, the cone has two cuspidal edges and the curve has two apparent cusps. When the quadric that cuts out the quartic goes through the vertex the residual consists entirely of the two double or cuspidal edges on which the apparent double points or apparent cusps lie, but for every other quadric that passes through the "quartic of the first kind," the residual is another "quartic of the first kind" similar to the original quartic; this may be shown as follows: since the quadric does not go through the vertex no edge or multiple can lie on it, and therefore the residual cannot break up, i. e. it must be a twisted quartic; moreover, every edge or multiple

* This is the number of common edges of its superior and inferior cones. Cayley, Collected Papers, V. p. 8.

edge meets the quadric twice and no more; then every double edge on which an apparent double point of the original quartic lies is met by the original quartic in two distinct points, and therefore the residual quartic must cross this double edge at the same two points, since there are two and only two branches of the complete intersection at these two points where the double edge meets the quadric; therefore, for every apparent double point of the original quartic there is an apparent double point of the residual quartic. The double or cuspidal edge, on which an actual double point or cusp of the original quartic lies, meets the quadric only once there, and must meet it at one more point, which is, therefore, a double point or cusp on the residual quartic. A cuspidal edge due to an apparent cusp on the original quartic meets the quadric in two consecutive points, and the residual quartic must pass through these two consecutive points, i. e. it has this cuspidal edge as a tangent and therefore the residual quartic also has an apparent cusp at this point. The residual quartic is therefore a "quartic of the first kind" similar to the original quartic. Each of these two "quartics of the first kind" considered as lying on the quadric, meets the generators of each system of the quadric in two points, and is therefore a 4_2 on the quadric; the formula for the number of intersections of two curves a_α and b_β on a quadric being $(a_\alpha, b_\beta) = a\,\beta + b\,\alpha - 2\,\alpha\,\beta$, the two quartics in question, considered as lying on the quadric, intersect in $(4_2, 4_2) = 8 + 8 - 8 = 8$ points; but on the cone these quartics are 4_1's, and, since they do not go through the vertex, formula (1) gives the total number of their intersections, so that regarding these quartics as lying on the cone they intersect in $(4_1, 4_1) = 4 + 4 - 4 = 4$ points. This illustrates what was said (p. 25) in reference to the point of crossing of two curves on a multiple line not counting as a point of intersection of those curves, considered as lying on the surface having the multiple line, when those curves lie on different sheets at this point of crossing. In the present case we have four such points, two on each of the two double or cuspidal edges on which the apparent double points or cusps lie; these four points count as points of intersection of the quartics considered as lying on the quadric, because the quartics lie on the same sheet of the quadric, but they do not count as points of intersection of the quartics, considered as lying on the cone, because these curves lie on different sheets of the cone at these points; these four points make up the difference in the number of intersections that the quartics have on the two surfaces.

The "quartic of the first kind" may lie on a cone with a tac-nodal edge formed by the union of two double or cuspidal edges; the quar-

tic then has an apparent tac-node equivalent to two apparent double points.

The quartic that lies on the cone having a triple edge, is a "quartic of the second kind;" for, if it were a "quartic of the first kind," we could pass a quadric through it and through the vertex; the triple line would then lie on the quadric and be a generator of one system; the generator of the other system that passes through the vertex would meet the cone four times at the vertex and at least once on the curve, and would therefore coincide with an edge of the cone; but an edge of the cone meets the quartic once only, and therefore the quartic would be met by the generators of one system of the quadric once only, and would not be a "quartic of the first kind" as supposed.

Every "quartic of the second kind" has three apparent double points (or cusps), and cannot lie on a quartic cone with fewer than three double or cuspidal edges; two of these may unite, forming a tac-nodal edge, or all three double edges may unite, forming a triple edge; on the tac-nodal edge the quartic has an apparent tac-node equivalent to two apparent double points, and on the triple edge the quartic has an apparent triple point equivalent to three apparent double points. Through every "quartic of the second kind" can be passed one and only one quadric, and, if the quartic lies on a cone with a triple edge, the quadric always passes through the vertex; for, the triple line meets the quadric three times on the quartic curve, and therefore lies on it, being a generator of one system of the quadric; the generator of the other system that passes through the vertex coincides with an edge of the cone, as we have seen, and therefore the residual consists of this edge and the triple edge. When the "quartic of the second kind" lies on a cone with three double (or cuspidal) edges, the quadric cannot go through the vertex (for if it did all three double or cuspidal edges would lie on it), and the residual is therefore another "quartic of the second kind" because it has an apparent double point (cusp) on each of the three double (cuspidal) edges; the points of crossing are the same as those of the original quartic, and the curves lie on different sheets at these points. Now, the generators of the quadric meet the cone four times, and, considering one system of generators, they must meet the cone three times on one quartic and once on the other quartic (since every "quartic of the second kind" on a quadric meets the generators of one system three times and those of the other system once), i. e. on the quadric, one of the quartics is a 4_3, and the other is a 4_1; therefore, considered as lying on the quadric, these quartics intersect in 10 points, $(4_3, 4_1) = 4 + 12 - 6 = 10$. But on the cone each

quartic is a 4_1, and these two quartics intersect in only 4 points, $(4_1, 4_1) = 4$. The six points, two on each double or cuspidal edge, where the branches of the two curves cross, do not count as points of intersection of the two quartics considered as lying on the cone, for the branches lie on different sheets of the cone at these six points, and this accounts for the difference in the number of intersections that the curves have on the two surfaces, — a further illustration of the principle already stated.

The different species of twisted quartics that lie on the different cones can be tabulated as follows, where δ is the number of actual double points, κ the number of actual cusps, h the number of apparent double points, k the number of apparent cusps, and T the number of apparent triple points.

Quartic Cone.			Quartic Curves.						
			First Kind.				Second Kind.		
Double Edges.	Cuspidal Edges.	Triple Edges.	δ	κ	h	k	h	k	T
2	0	0	0	0	2	0			
1	1	0	0	0	1	1			
0	2	0	0	0	0	2			
2	1	0	0	1	2	0	2	1	0
			1	0	1	1			
1	2	0	1	0	0	2	1	2	0
			0	1	1	1			
3	0	0	1	0	2	0.	3	0	0
0	3	0	0	1	0	2	0	3	0
0	0	1					0	0	1

5. Salmon* has divided twisted quintics into four groups, viz. group (I), having four apparent double points, group (II), having five appar-

* Geom. of Three Dimensions, § 352.

ent double points, and groups (III) and (IV), having six apparent double points. Now, from an ordinary point on any curve of order m, the number of apparent double points of the curve is $h - m + 2$,* where h is the number of apparent double points of the curve from an arbitrary point; therefore, since every twisted quintic on a quartic cone has one branch through the vertex, the number of apparent double points from the vertex, i. e. the number of double edges of the quartic cone, is $h - 3 \geqq 1$; moreover, since any twisted quintic can be cut out by a cubic monoid, the six lines of the monoid that pass through the vertex must count for seven, the order of the residual, and therefore the cone has at least one double (or cuspidal) edge with which one of these six lines coincides; therefore there is no quintic curve on the non-singular cone. There is a twisted quintic, which is not a special case of any of the groups given by Salmon, that has only three apparent double points, but it has an actual triple point, where the three tangents do not lie in the same plane, and the quartic cone on which it lies has a triple edge due to this actual triple point. All the quartic cones, except the non-singular cones, have species of twisted quintics on them, and these may be tabulated in the same way as the twisted quartics.

We have seen that any twisted sextic can be cut out by a cubic monoid, and, since the residual is of order six, the six lines of the monoid that pass through the vertex may be six edges of the cone, and therefore the non-singular cone, as well as each of the other cones, may have twisted sextics on it.

Any twisted curve of order 7 can be cut out by a quartic monoid which has 12 lines that pass through the vertex, 9 of which may be edges of the cone, forming the total residual, and therefore a quartic cone of any group has on it some species of twisted curve of order 7. For $a \geqq 8$ we have $\alpha \geqq 2$ for some species of a_α, and therefore when $a \geqq 8$, a quartic cone of any group has on it some species of a_α.

* Salmon's Geom. of Three Dimensions, § 330, example 2.

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ON SUPPOSED MEROSTOMATOUS AND OTHER PALEOZOIC ARTHROPOD TRAILS, WITH NOTES ON THOSE OF LIMULUS.

By Alpheus S. Packard.

PALEONTOLOGICAL NOTES, NO. VI.

ON SUPPOSED MEROSTOMATOUS AND OTHER PALEOZOIC ARTHROPOD TRAILS, WITH NOTES ON THOSE OF LIMULUS.

By Alpheus S. Packard.

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Trails or tracks evidently made by paleozoic arthropods have occurred most abundantly in the Potsdam sandstone (Cambrian) of Canada and New York, also in the Hudson River or Cincinnati stage of the Ordovician Period. We have now to add descriptions of tracks of a similar nature from the Chemung stage (Upper Devonian) and from the Upper Carboniferous. We will give the name *trail* to the entire series of footprints, and restrict the word *track* to the individual footprints. The trails discovered by Logan, and carefully described by Professor R. Owen,* were very large, being six inches wide and several feet long, and were evidently made by some large trilobite (as first suggested by Dana) with a caudal spine, as there is a well-marked median furrow. Whether the trilobite was a Paradoxides or not is uncertain, because the species of this genus are without a definite caudal spine, such as is to be seen in Dalmanites and certain other trilobites of a later period than the Cambrian. But aside from this the tracks, in sets of seven and eight, seem most probably to have been made by an arthropod with numerous pairs of jointed cylindrical legs, such as we now know, through the researches of Walcott and of Beecher, trilobites possessed. Professor Owen described six species of the tracks, for which he proposed the generic name of Protichnites, but we venture to suggest that it is not improbable that they were all made by a single species of trilobite, as observation has taught us that Limulus may make tracks of very dissimilar shape. We would suggest that to trails consisting of sets of several, or as many as

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* Journal Geolog. Soc. London, VIII. pp. 199, 214. 1852.

These trails, *Protichnites septem-notatus* Owen, are figured on a reduced scale in Dana's Manual of Geology, Fig. 256; and *P. octonotatus* Owen in the new edition of Bronn's Lethæa geognostica.

7 or 8, individual tracks, the term Protichnites be restricted. Logan's *Climactichnites wilsoni*, six and a half inches wide and thirteen feet long, also from the Potsdam sandstone, which Dana suggested may have been made by a large trilobite,* seems to be such. There is an interrupted median furrow; the oblique furrows were probably made by the legs, and the lateral furrow bounding the track is much like that made by the cheeks or sides of the head of Limulus.

We now come to similar but less complex tracks described by O. C. Marsh, † also from the Potsdam sandstone near Port Kent, N. Y. This trail was about six feet long, and the tracks were separated from each other "by a space of about one and three-fourths inches, and having an extreme width between their outer edges of two and a half inches." In this trail there is no median furrow, no lateral ridge, and here and there are double tracks, as if they were footprints made by a second anterior pair of feet. The track has a decided merostomatous appearance, but was probably made by a trilobite, as there are no Limuloid merostomes known to have existed in the Cambrian, and the track could scarcely have been made by an Eurypterid.

The next set of paleozoic trails are those described by Miller and Dyer ‡ in 1878, in a fine hard shale of the Cincinnati's stage of the Ordovician Period at Cincinnati. The originals are in the Museum of Comparative Zoölogy at Cambridge, Mass., and I am indebted to Dr. R. T. Jackson for the privilege of examining them. One of them is similar to that described below from Providence, but the trail is twice as wide, and the tracks not so wide. They were perhaps made by a trilobite; there is no median furrow, or lateral ridges. §

The trails of Limulus polyphemus. — Figs. 1, 2 (one-third natural size). The trail made by this merostome has been described and figured by the late Sir J. W. Dawson in the Canadian Naturalist, VII. p. 271. He gives three interesting figures of the trails left by a single small Limulus four inches wide on a sandy shore. In each of his figures the median furrow is distinct, but the lateral marks are furrows "with slight ridges exterior to these," while my example left only a ridge. The

* Manual of Geology, p. 189 (first ? edition), Fig. 259.

† Amer. Journ. Sc. and Arts, XLVIII. July, 1869. Plate.

‡ Journ. Cincinnati Natural History Society, 1878.

§ The trails figured by Emmons (Agriculture of New York, I.) as *Nereites jacksoni pugnus* and *loomisii*, appear to be Annelid trails, and none of those figured by James Hall (Paleontology of New York, II. Pls. 13–16) seem to have been made either by trilobites or merostomes.

footprints were slightly oblique series of four punctures, or pits, "deepest behind, in which the four marks left by the nails of the posterior feet were most prominent, and sometimes the only marks seen."

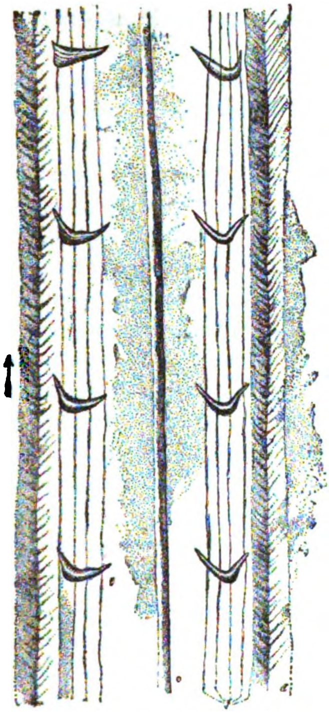

FIGURE 1.

FIGURE 2.

"When the Limulus creeps on quicksand, or on sand just covered with water, so that its body is partly water-borne, it appears principally to use its ordinary walking feet, and the footprints then resolve themselves into a series of longitudinal scratches after the manner of *Protichnites lineatus*." . . .

"When placed in shallow water, just covering the body, the creature used its flat abdominal swimming feet, and though the impression made was very faint, and not readily observed under water, it was obviously very different from those before mentioned, agreeing with them only in the lateral and median grooves, while between these were series of furrows extending obliquely from each side of the middle groove, and re-

sembling ripple marks (Fig. 3). These were produced by the sand swept up by the swimming feet." Dr. Dawson then compares the trail represented by his Fig. 3 with Logan's Climactichnites, and they are remarkably similar, except that the oblique furrows made by the legs between the median and lateral ridges are directed in the reverse direction.

Of the tracks afterwards described and figured by Dr. Dawson * from the upper Carboniferous of Nova Scotia, none seem to me to be referrible to trilobitic or merostomatous trails. *Protichnites carbonarius*, as already remarked in these Proceedings, † appear to have been made by a crustacean, and we have referred them to a distinct genus, *Ostrakichnites*.

Some years ago I made some experiments with small Limuli by placing one in a shallow tin pan, in which the sand was about half an inch deep, and the water not deep enough to entirely cover the body. The animal, so far as I can now remember, used its ambulatory feet in walking, while the swimming or abdominal legs were partially used. The result may be seen in Fig. 1. The king-crab was about four inches (10 cm.) in width. The trail it made consisted, besides the tracks themselves, of an outer ridge made by the outer edge of the head or carapace; this ridge (*d*) was about 15 mm. in width, and was due to the heaping up of the fine sand; in section it would be low conical; one would suppose that the action of the edge of the head would make a furrow rather than an elevated ridge.

The tracks (*t*) were opposite, and quite regularly concavo-triangular, the apex of the triangle rounded, and directed backwards, the sand being pushed slightly up on the posterior edge of the track.

The tracks of each side were directly opposite each other, and those of each pair directly in line with those of the pair in front. It was noticed that the distance apart of the tracks varied with the rapidity of the half-walking, half-swimming movements of the animal. It was seen that the tracks were made by the hindermost, or sixth pair, of limbs only, no impression being left in the sand by the feet in front. The triangular shape of the track was due to the spreading out of the two spatulate spines of the last segment of the leg. It should be observed that the distance apart, outside measurement, of the tracks is about two-thirds that of the entire trail.

* Impressions and footprints of aquatic animals and imitative markings on carboniferous rocks. Amer. Journ. Sc. and Arts, 3d Series, V. Jan. 1873, pp. 16–24, Figs. 1–5. Also Acadian Geology, 2d edit. Supplement. 1878.

† XXXV. April, 1900, p. 403.

The four narrow furrows (*f*) intersecting the tracks were made by the lateral abdominal spines, which are bent down and trail in the mud or sand when the animal is walking or moving over the bottom. The large, deep, median furrow (*c*) was made by the caudal spine; it was continuous, uninterrupted, during the continuous forward movements of the animal.

Another trail is represented by Fig. 2. It will be seen that it presents no resemblance to the other. Unfortunately I did not make any notes as to the relations of the animal to the bottom. So far as I can remember it was a smaller individual, and probably it moved rapidly. The indentations on the margin of the trail were evidently made by the feet, while the series of median furrows were made by strokes of the caudal spine. The trail was 3.50 cm. wide.

The tracks of living terrestrial Isopod Crustaceans. — Fig. 3. In this connection it was interesting to ascertain the nature of the tracks made by Crustacea so much like trilobites in general shape as our terrestrial Isopods. One of our common Armadillo was captured, its feet inked, and it was then set free and allowed to "make tracks" on a sheet of paper. It will be remembered that the Isopods have seven pairs of ambulatory legs, the extremities of which end in a single sharp point. The width of the body is from 4 to 5 mm. It was noticed that the crustacean in running put down the feet of each pair at the same time, and that the legs, and especially the pointed extremities, were perpendicular to the surface over which it ran.

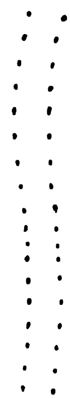

FIGURE 3.

The trail thus made was a very simple one, being a double row of slightly elongated dots, the individual tracks of each pair being exactly opposite to each other, as seen in the figure. When the feet dragged the dots became lines. The trail is also nearly of the same width as the body itself, though a little narrower rather than wider.

A specimen of our common *Porcellio scaber* was also compelled to undergo similar treatment and like evolutions with the same result. The trail differed in no essential respects from that of the other Isopod.

It will be of much interest to experiment with macrurous and brachyurous Crustacea, in order that the results may throw light on the numerous tracks in the Triassic beds of the Connecticut Valley described by Hitchcock in his "Ichnology."

Merostomichnites beecheri n. sp. Fig 4. This trail is in a fine shaly sandstone of the Chemung beds at Warren, Pa. It covers an area

3 cm. long and about 9 mm. wide. It is straight and short. The individual tracks are opposite each other, as in those of Limulus. The animal must have leaned more to the right side, as the tracks on this side are larger, deeper, and much more perfect than on the left side. The most perfect ones are in shape almost exactly like those made by Limulus when half walking and half swimming in very shoal water. A typical track may be described as forming a low triangle, the apex pointing backward; it is hollow, the interior forming a hollow triangle surrounded by a raised ridge.

There are six pairs of tracks, with traces of a seventh. The width of the trail is 9 mm., but probably if the entire trail were perfect on the left side it would have measured about 10 mm. in width. The tracks are opposite to each other. The largest and best marked individual track is 5–6 mm. wide and 3 mm. deep (or long) from in front to the apex or hinder part. The tracks of each pair are very near to each other, and those in the front part of the trail tend to be united into a simple transverse ridge.

There are no secondary tracks in between the others, and in this respect the track differs from that of *M. narragansettensis*, and resembles that of Limulus.

The original of this track is in the paleontological collection of the Peabody Museum of Yale University. I am indebted to the kindness of Professor C. E. Beecher, the curator, who did me the favor to send me an excellent cast, from which the above description has been made. Professor Beecher informs me that in the beds of the Chemung group at Warren, Pa., there are no remains of trilobites; and he expressed his belief that the tracks were those of some merostome. It is to be observed that there is no median furrow or trail made by a tail or caudal spine, and no furrow or ridge made by the edge of the body or carapace. The merostome which made it most probably had no caudal spine. And yet the tracks are otherwise very similar to those of Limulus. It may be observed that all the Eurypterida are provided with a telson, either broad or narrow and spine-like, and their trails would evidently include a furrow made by such a spine. The Limulidae were represented in the Devonian by *Protolimulus eriensis* Williams ("associated with typical Chemung fossils"). Was this track made by a young individual of this genus, with the caudal spine too short to make a trail? If not, was it made by a Bunodes, which lived in the Upper Silurian of Europe, but has not yet been discovered in America, and had no caudal spine? But Bunodes would perhaps have left a lateral furrow made by the broad thin edge of

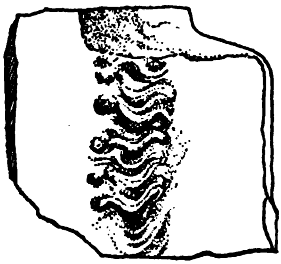

FIGURE 4.

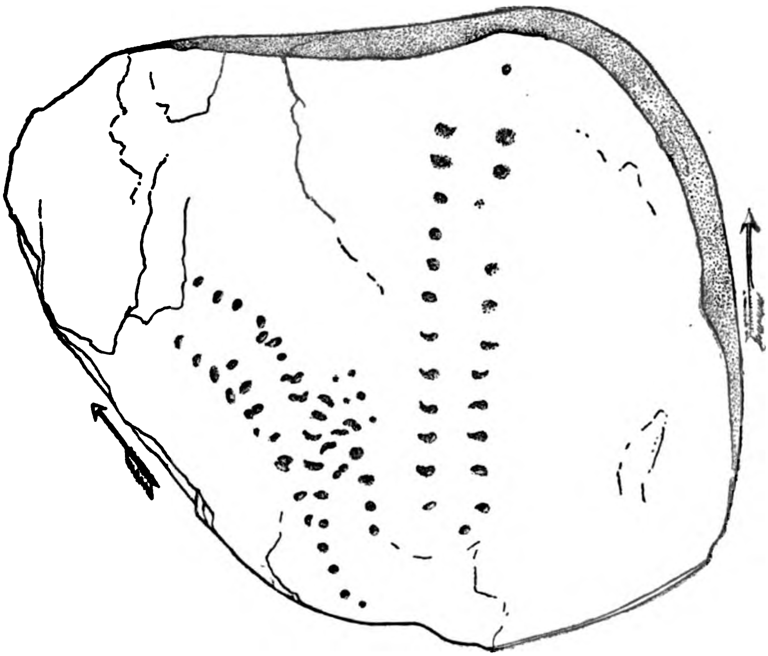

FIGURE 5.

its elliptical body. The trail seems to indicate the occurrence of a merostome of a group not represented by any known fossil genus, unless it should prove to be a young Protolimulus.

Merostomichnites narragansettensis (Pack.). Fig. 5. Proc. Amer. Acad. Arts and Sci. XXXV. No. 20, April, 1900, p. 402. Three trails of this species were discovered by a member of my geological class, —Mr. H. H. Mason, of the class of 1900,—and kindly given to me, while doing field work under my direction in Providence, R. I., just north of the city and of the North Burying Ground. The trails occurred in a rounded pebble of dark arenaceous shale picked up from the mass of water-worn gravel and boulders constituting the body of a large rounded kame. It was split in two, so as to show the impressions and the relief of the tracks. The subglacial deposits at this point are derived from a region a few miles a little east of north, probably in the vicinity of South Attleboro, though I have not seen beds of this peculiar blackish sandy shale in place.

There are three trails, — one separate, and the two others crossing each other. The long separate series is nearly straight, 6.50 cm. in length ; the other trail is sinuous, and is crossed by a third, shorter trail. The width of each trail is the same, being about 12 mm. outside measurement. The distance between the individual tracks of the same pair is about 9 mm., that between the footprints on the same side varies from about 2 mm. to about 4 mm.

The tracks are opposite and not alternate. Along most of the length of the trail there is but a single series of tracks on a side, but in portions of the entire trail the footprints are double, there being an inner and an outer set on each side. If we select four of the tracks in a place where they are double, it will be seen that they are arranged in a very low trapezoid; while the space between the two outside tracks is 9 mm., that between the two inner, a little in advance, is 5 mm.

The individual tracks forming the trails are of quite uniform shape, the best marked ones being transversely oval or crescentic in outline, the mud having been pushed back by the animal's feet so as to leave a crescentic ridge, the concavity pointing forward. The size of the impression in transverse diameter is about 3 mm., the longitudinal diameter 1.5, i. e. the tracks are about twice as broad as long. Thus they are not linear, and more or less parallel to the main series of tracks, as in those referred to the decapod crustacea. In two or three cases the tracks are connected by a slight ridge curved forward in the direction the animal moved.

While these tracks are certainly not Isopod tracks, they with still more certainty cannot be referred to impressions made by the feet of insects, which are always alternate, as in hexapod insects the legs of each pair are raised and put down alternately. The Providence carboniferous tracks were evidently made by an arthropod of the same group as Limulus, as the tracks are opposite, and in general shape like those of Limulus, as may be seen by Fig. 1. The present tracks differ from those of Limulus in the absence of a caudal spine trail-mark, and in the fact that an additional anterior pair of feet made impressions. Trilobites are not known to exist in our Upper Carboniferous associated with Limulus. Limuloids of the genus Prestwichia with a short caudal spine exist in considerable numbers in the Upper Carboniferous of Mason Creek, Illinois, and in the Upper Carboniferous beds of Pennsylvania, though from a horizon higher than that of the Mason Creek beds. As the genus Belinurus has a very long caudal spine, and there are no traces of a median furrow in our trails, that genus should be ruled out as the author of these tracks. Now the adult Prestwichia is about two inches in diameter and its caudal spine nearly half an inch in length. It is, however, well known that in the freshly hatched Limulus, and even after the first moult, and when the creatures are half an inch in diameter, the caudal spine is very short, too much so, probably, to leave a trail or median furrow.

The Providence trails are considerably less than half an inch in diameter, and reasoning by analogy, and also in part by exclusion, it seems not impossible that these trails are the footprints of a young Prestwichia a little less than half an inch in diameter, with too short a caudal spine to leave a furrow.

This conclusion is interesting as suggesting the occurrence of these Limuloids in the Narragansett basin during the later part of the Carboniferous Period. These tracks are so similar to those of the Chemung beds above described that they were probably made by Merostomes of the same family or genus, and may be referred to Merostomichnites rather than to Protichnites.

The possibility that these trails could have been made by an Eurypterid seems excluded by the absence of a median furrow, or of any prints made by the large paddles of the hind feet, or by the paddles and chelae of the first pair of feet of such a form as Pterygotus.

Brown University.

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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY
OF HARVARD COLLEGE.

CERTAIN DERIVATIVES OF METADIBROMDINITROBENZOL.

BY C. LORING JACKSON AND W. P. COHOE.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

CERTAIN DERIVATIVES OF METADIBROMDINITRO-BENZOL.

By C. Loring Jackson and W. P. Cohoe.

Presented December 13, 1899. Received June 4, 1900.

The dibromdinitrobenzol melting at 117°.4 was made by Körner in his classical research on Isomerism of the Aromatic Compounds with Six Atoms of Carbon,* but its constitution has not been determined with certainty. Nietzki and Schedler † in a recent paper have proved that the dichlordinitrobenzol melting at 103° has the structure Cl_2 1. 3. $(NO_2)_2$ 4. 6, and as this substance is made from the action of fuming nitric acid on metadichlorbenzol, just as the dibrom compound is made from metadibrombenzol, there is good reason to believe that they have the same constitution; but we thought it necessary to prove that this was the case before we studied this dibromdinitrobenzol further. For this purpose we heated the substance with aniline, and obtained the dianilidodinitrobenzol melting at 186°, which Nietzki and Schedler had obtained from their dichlordinitrobenzol; the dibrom substance therefore has the structure Br_2 1. 3. $(NO_2)_2$ 4. 6. If aniline acted on the dibromdinitrobenzol in the cold, a bromanilidodinitrobenzol, $C_6H_2BrC_6H_5NH(NO_2)_2$, melting at 157° was obtained, and this occurs in a yellow and in a red modification which seem to differ in crystalline form as well as in color. This seems to be a case of dimorphism, as the two forms pass into each other with great ease. The yellow form is converted into the red by crystallization from benzol, the red into the yellow by heating to 135°. Similar phenomena have been observed in the cases of anilidotrinitrophenyltartronic ester ‡ and trianilidodinitrobenzol. §

* Gazz. Chim. 1874, 305.

† Ber. d. chem. Ges., XXX. 1666 (1897).

‡ Jackson and Bentley, These Proceedings, XXVI. 83.

§ Jackson and Herman, Ibid. XXVII. 253.

After the constitution of the 1. 3. 4. 6 dibromdinitrobenzol had been determined, we studied the action of sodic ethylate upon it, in the hope of encountering the replacement of bromine by hydrogen under the action of this reagent, which has been studied for some years in this Laboratory. But no such behavior was observed; the action ran in the normal way, resulting in the formation of the dinitroresorcine diethylether melting at 133°, discovered by Warren and one of us,* and proved to have the symmetrical structure by Koch and one of us †; so that this observation confirms the determination of the constitution of this body by the action with aniline.

Sodic phenylate converted the dibromdinitrobenzol into diphenoxydinitrobenzol, which melts at 129°. The action of sodic malonic ester was tried on this compound to determine whether the phenoxy groups could be replaced by the malonic ester radical $CH(COOC_2H_5)_2$; as it has been found ‡ that the best way to make dichlordimalonicesterquinone $C_6Cl_2[CH(COOC_2H_5)_2]_2O_2$ is by treating dichlordiphenoxyquinone with sodic malonic ester, and we wished to see whether the nitro groups would produce the same effect as the oxygen atoms of the quinone in promoting the replacement of the phenoxy groups by malonic ester radicals. We found that phenol was eliminated when the diphenoxydinitrobenzol was treated with sodic malonic ester, and from the very unmanageable product a sodium salt was obtained which contained an amount of sodium corresponding to $C_6H_2OC_6H_5CNa(COOC_2H_5)_2(NO_2)_2$; so that we feel justified in assuming that the reaction has consisted in the replacement of the phenoxy by the malonic ester group.

The dibromdinitrobenzol, when reduced with zinc dust and acetic acid, gave a dibrommetaphenylene diamine, which was identical with that melting at 135° obtained by the action of bromine on metaphenylene diacetamid. § It follows from our preparation of this base that it has the constitution Br_2 1. 3. $(NH_2)_2$ 4. 6.

In all this work we have been careful not to approach too near to the field reserved by Nietzki and Schedler in their paper on dichlordinitrobenzol.

* These Proceedings, XXV. 170.

† Ibid. XXXIV. 134.

‡ Jackson and Grindley, Ibid. XXX 425.

§ Jackson and Calvert, Ibid. XXXI. 150.

Preparation of Metadibromdinitrobenzol.

Monobromacetanilid was first made by passing a stream of air laden with the vapor of bromine through five litres of water in which fifty grams of acetanilid were suspended. The end of the reaction was determined by the appearance of a lasting yellow color in the liquid and a distinct change in the appearance of the solid. In all our attempts to convert this product into the dibromacetanilid by the action of liquid bromine on it when suspended in water, we observed the formation of a considerable amount of symmetrical tribromaniline (NH_2 1. Br_3 2. 4. 6.), produced undoubtedly by the action of bromine on the free base proceeding from the saponification of some of the bromacetanilid by the hydrobromic acid formed in the reaction. The monobromacetanilid was accordingly filtered out, and after being dried, suspended in glacial acetic acid or chloroform, to which a little more than the calculated amount of bromine was then added drop by drop. This method gave an excellent yield of the dibromacetanilid with little trouble.

The dibromacetanilid was saponified by boiling it with sulphuric acid of specific gravity 1.44 in a flask with a return condenser, until the solution of the solid, which was usually accompanied by a darkening in color, showed that the reaction was complete. The liquid was then allowed to cool, when most of the dibromaniline crystallized out, and what remained in solution was precipitated by the addition of a large quantity of water.

To remove the amido group, 100 grams of the dibromaniline were dissolved in a mixture of 300 c.c. of alcohol and 120 c.c. of benzol, to which 20 c.c. of sulphuric acid had been added; the mixture was heated in a flask on the steam bath, and 60 grams (a large excess) of solid sodic nitrite added as fast as the reaction would permit. The contents of the flask, which had taken on a reddish color, were boiled for an hour, and then allowed to stand over night, after which a large quantity of water was added, and the precipitated oily liquid distilled over with steam. A small amount of tribrombenzol is usually present, which appears as a solid in the condenser toward the end of the distillation with steam; it is well to stop the distillation as soon as this solid appears. The distillate with steam was dried with calcic chloride and distilled, collecting for use the fraction boiling from 210° to 225°. A small additional amount of dibrombenzol was obtained by extracting with ether the aqueous portion of the steam distillate, but the increase of the yield in this way was so small that this extraction was hardly worth while.

The dibrombenzol was converted into dinitrodibrombenzol by boiling

it with fuming nitric acid of specific gravity 1.52, or better a mixture of this acid and sulphuric acid. As soon as the oil had dissolved in the acid, the reaction was complete; the boiling was stopped, and the product precipitated by pouring the acid liquid into a large quantity of cold water. The yellow crystals thus obtained were purified by crystallization from alcohol, until they showed the constant melting point 117°.

Determination of the Constitution of Metadibromdinitrobenzol by the Action of Aniline.

Two grams of the dibromdinitrobenzol melting at 117° were heated with an excess of aniline on the steam bath for half an hour. At the end of this time the excess of aniline was removed by treatment with dilute hydrochloric acid, and the yellow residue, after being washed thoroughly with water, was recrystallized from a mixture of alcohol and benzol until it showed the constant melting point 185°, which is essentially identical with 186°, that of the dianilidodinitrobenzol prepared from dichlordinitrobenzol by Nietzki and Schedler.* As they established the constitution $(NHC_6H_5)_2$ 1. 3. $(NO_2)_2$ 4. 6 for this body, the dibromdinitrobenzol belting at 117° must have the corresponding structure Br_2 1. 3. $(NO_2)_2$ 4. 6.

Action of Aniline on Symmetrical Dibromdinitrobenzol in the Cold: Bromanilidodinitrobenzol.

Two grams of the dibromdinitrobenzol cooled by a freezing mixture were moistened with aniline, and the mixture was allowed to stand packed in ice for twelve to eighteen hours. The excess of aniline was then removed by dilute hydrochloric acid, and the dense yellow residue, after thorough washing with water, was purified by crystallization from alcohol and benzol until it showed the constant melting point of 157°, when it was dried at 100°, and analyzed, with the following result: —

I. 0.0994 gram of the substance gave by the method of Carius 0.0558 gram of argentic bromide.

II. 0.2138 gram of the substance gave 0.1229 gram of argentic bromide.

	Calculated for $C_6H_2BrC_6H_5NH(NO_2)_2$	Found. I.	II.
Bromine	23.67	23.89	24.46

* Ber. d. chem. Ges., XXX. 1668 (1897).

Properties of Bromanilidodinitrobenzol, $C_6H_2BrC_6H_5NH(NO_2)_2$(Br 1. C_6H_5NH 3. $(NO_2)_2$ 4. 6.).

This substance crystallizes from a mixture of benzol and alcohol, sometimes in much modified short and thick flat prisms apparently of the monoclinic system, resembling certain crystals of felspar; at other times in rhombic plates occasionally with some of the angles slightly bevelled, which pass into forms like rhombohedra; all of these crystals have a full golden yellow color. Other crystals were distinguished from these by their brilliant red color and by appearing in square prisms modified on one of their angles or on two opposite angles. From these two colors, red and yellow, and the difference at least in crystalline habit, if not really in crystalline form, we infer that the substance appears in two closely related modifications. The yellow form, in which the substance is obtained from its preparation, becomes gradually converted into the red by crystallization from a mixture of alcohol and benzol, but several crystallizations are necessary to make this conversion complete. If, however, the yellow form is dissolved in benzol alone, the solution deposits, as it evaporates, a red oil, which on stirring solidifies to the red crystals. All the other common organic solvents except the alcohols also convert the yellow into the red form by a single crystallization. On the other hand, if the red crystals are heated in an air bath, they begin to assume a yellow color at 110°, and are completely converted into the yellow form at 135°; this conversion is attended with no change in weight. The substance melts at 157°, forming a red liquid, which, when cooled and stirred, solidifies to the yellow modification. It is obvious that the melting point given above is that of the yellow form, since the red is converted into the yellow at 135°. The bromanilidodinitrobenzol is freely soluble in benzol; soluble in toluol or chloroform; slightly soluble in ether, acetone, amyl alcohol, or hot ethyl alcohol. The best solvent for it is a mixture of benzol and alcohol.

Determination of the Constitution of Metadibromdinitrobenzol by Treatment with Sodic Ethylate.

One gram of the dibromdinitrobenzol melting at 117° was mixed with an excess of sodic ethylate prepared by the action of sodium on a considerable excess of absolute alcohol, and after the mixture had stood for some time at ordinary temperatures, the excess of alcohol was allowed to evaporate spontaneously. The residue, after repeated washings with

hot water, was purified by crystallization from a mixture of ligroin and benzol, when it was found to melt at 133°, the melting point of the dinitroresorcine diethylether discovered by Warren and one of us,* which it also resembled in crystalline form. As Koch and one of us† have proved that this dinitroresorcine diethylether has the constitution $(OCH_3)_2$ 1. 3. $(NO_2)_2$ 4. 6, it follows that the dibromdinitrobenzol melting at 117° has the constitution Br_2 1. 3. $(NO_2)_2$ 4. 6, — a result which confirms that already obtained from the action of aniline.

Action of Sodic Phenylate with Symmetrical Dibromdinitrobenzol.

The sodic phenylate for this experiment was prepared by adding five grams of powdered sodic hydrate to enough melted phenol to make a pasty mass. While this was still in the viscous state, five grams of the dibromdinitrobenzol were added little by little with constant stirring, the beaker containing the mixture being kept cool with ice water. The product, a dark brown solid mass, was treated with water, filtered, and the insoluble portion recrystallized either from slightly dilute alcohol, or from a mixture of benzol with a large excess of ligroin, until it showed the constant melting point 129°, when it was dried *in vacuo*, and analyzed, with the following results: —

I. 0.2494 gram of the substance gave on combustion 0.5563 gram of carbonic dioxide and 0.0903 gram of water.

II. 0.3746 gram gave on combustion 0.8457 gram of carbonic dioxide. The water was unfortunately lost.

	Calculated for $C_6H_2(OC_6H_5)_2(NO_2)_2$.	Found. I.	II.
Carbon	61.38	60.82	61.59
Hydrogen	3.41	4.02	

The method of making sodic phenylate given above was adopted because in alcoholic solution the sodic phenylate gave principally the dinitroresorcine diethylether, and in aqueous solution there was no action until high temperatures were reached, and then the yield was unsatisfactory.

* These Proceedings, XXV. 170.

† Ibid., XXXIV. 134.

PROPERTIES OF THE DINITRORESORCINE DIPHENYLETHER, $C_6H_2(OC_6H_5)_2(NO_2)_2.((OC_6H_5)_2\ 1.\ 3.\ (NO_2)_2\ 4.\ 6.)$.

This substance, when crystallized from a mixture of benzol and alcohol, forms slender white prisms terminated by one slanting plane, or, when better developed, by two planes meeting at a very obtuse angle and modified by several smaller ones, so that a blunt end is formed. It melts at 129°. It is freely soluble in benzol; soluble in cold toluol or chloroform, or in alcohol, ligroin, or acetone when these solvents are hot; slightly soluble in ether or amyl alcohol. The best solvent for it was either dilute alcohol, or ligroin containing a little benzol.

Some experiments were tried to determine whether the phenoxy groups in the diphenoxydinitrobenzol could be replaced by malonic ester radicals ($CH(COOC_2H_5)_2$), as a replacement of this sort had been observed in the case of dichlordiphenoxyquinone.* The solid diphenoxydinitrobenzol was dissolved in an alcoholic solution of sodic malonic ester, and the mixture allowed to stand at ordinary temperatures over night; afterward it was treated with dilute sulphuric acid, which precipitated an oil, and showed that phenol had been set free by the strong smell of this substance. The oily precipitate, after washing with water, was extracted with ether, which removed from it a pale yellow oily substance; but as this did not solidify even after standing for several months, we tried to determine its nature by the analysis of a salt. A specimen of the oil was dissolved in alcohol and treated with an aqueous solution of sodic hydrate, which threw down a bright red precipitate; this was washed with benzol, dried *in vacuo*, and analyzed, with the following results:—

I. 0.1383 gram of the substance gave 0.0191 gram of sodic sulphate.
II. 0.1476 gram of the substance gave 0.0228 gram of sodic sulphate.

	Calculated for $C_6H_2(NO_2)_2OC_6H_5CNa(COOC_2H_5)_2$.	Found. I.	II.
Sodium	5.23	4.47	5.01

The results of these analyses, in connection with the elimination of phenol, prove that the reaction has run as was expected. The phenoxydinitrophenylmalonic ester separated from the salt as an oil, and therefore we did not think it worth while to attempt a more careful study of it.

* Jackson and Grindley, These Proceedings, XXX. 425.

Reduction of Symmetrical Dibromdinitrobenzol with Zinc Dust and Acetic Acid.

Twenty grams of zinc dust were placed in a flask fitted with a Bunsen valve and connected with a carbonic dioxide generator, acetic acid of eighty-five per cent was added, and then five grams of the dibromdinitrobenzol in small portions at a time, as under these conditions the reaction ran quietly and smoothly, although accompanied by blackening in every case. The reduction was carried on at first in the cold, but toward the end of the operation the mixture was heated gently on the steam bath. After two hours the reaction was complete, when the insoluble portion was filtered out, and extracted with dilute alcohol, which upon cooling deposited crystals melting even in the crude state at 131°. The filtrate from the insoluble reduction products was treated with an excess of sodic hydrate sufficient to dissolve the zinc salts, the precipitate formed in this way filtered out, and extracted with hot dilute alcohol, which gave another portion of the crude product melting at 131°. After purification by crystallization from alcohol the melting point became constant at 134°; it was dried *in vacuo*, and analyzed with the following result: —

0.1407 gram of the substance gave by the method of Carius 0.1976 gram of argentic bromide.

	Calculated for $C_6H_2Br_2(NH_2)_2$.	Found.
Bromine	60.15	59.78

This dibromphenylene diamine melts essentially at the same point (135°) as that prepared by S. Calvert and one of us* from metaphenylene diacetamide and bromine. It also crystallizes like this in white needles, which turn brown on exposure to the air. As the constitution of our dibrombinitrobenzol is Br_2 1. 3. $(NO_2)_2$ 4. 6, it follows that this dibrommetaphenylene diamine must have the corresponding constitution Br_2 1. 3. $(NH_2)_2$ 4. 6.

* These Proceedings, XXXI. 150.

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ON THE CONTINUITY OF GROUPS GENERATED BY INFINITESIMAL TRANSFORMATIONS.

By Stephen Elmer Slocum.

ON THE CONTINUITY OF GROUPS GENERATED BY INFINITESIMAL TRANSFORMATIONS.

By Stephen Elmer Slocum,
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Presented by Henry Taber, May 9, 1900. Received June 20, 1900.

§ 1.

The publication of the results of Professor Sophus Lie's investigations in the theory of finite continuous groups, embodied in papers appearing from 1870 to 1898, chiefly in the "Archiv for Mathematik og Naturvidenskab" and the "Forhandlingar i Videnskabs Selskabet i Christiania," and the systematic presentation of his theory in six large volumes, published during the years 1888–1893, opened to mathematicians a new and exceedingly rich field of investigation. As a creator and pioneer in this field, Professor Lie's aim was to outline his theory as broadly as possible, not stopping to obtain entirely rigorous demonstrations of his theorems; and it is not surprising to find that certain of these theorems, and of the fundamental conceptions of his theory, require modification. Thus it appears from a discovery of Study's, mentioned below, that the chief theorem of Lie's theory holds, in general, only in the neighborhood of the identical transformation, and, as a consequence of this fact, that the conception of isomorphism, as developed by Lie, requires modification.

The chief theorem of Lie's theory is that r independent infinitesimal transformations,* whose symbols are

$$X_i \equiv \sum_1^n{}_k\, \xi_{ik}\,(x_1 \ldots x_n)\, \frac{\partial}{\partial x_k}$$
$$(i = 1, 2 \ldots r)$$

(where the ξ's are analytic functions of n independent variables $x_1 \ldots x_n$) generate an r-parameter (*r-gliedrige*) group, in which each transformation

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* Lie terms the symbols of infinitesimal transformation $X_1 \ldots X_r$ *independent* if the ξ's satisfy no linear homogeneous relations of the form

$$e_1\,\xi_{1i}\,(x) + \ldots + e_r\,\xi_{1r}\,(x) \equiv 0$$

simultaneously for $i = 1, 2 \ldots n$, with coefficients e independent of the x's.

is generated by an infinitesimal transformation of the group, if and only if the $X_1 \ldots X_r$ fulfil relations of the form

$$(X_j, X_k) \equiv \sum_1^r {}_s c_{jks} X_s$$
$$(j, k = 1, 2 \ldots r),$$

where (X_j, X_k) denotes the alternant $X_j X_k - X_k X_j$, and the coefficients c_{jks} are quantities independent of the x's.*

In Volume XXXV. of the "Proceedings of the American Academy of Arts and Sciences," pp. 239 *et seq.*, I pointed out an error in the demonstration of what Lie calls the first fundamental theorem,† upon which he bases the demonstration of his chief theorem. This error consists in neglecting conditions imposed at the outset upon certain auxiliary quantities $\mu_1, \mu_2 \ldots \mu_r$, introduced in the course of the demonstration. Thus in the "Continuierliche Gruppen," pp. 372–376 (and substantially in "Transformationsgruppen," III. pp. 558–564), Lie proceeds as follows: Being given at the outset a family with an ∞^r of transformations T_a, defined by the equations

$$x'_i = f_i(x_1, \ldots x_n, a_1, \ldots a_r)$$
$$(i = 1, 2 \ldots n),$$

containing the identical transformation, and such, moreover, that the x''s satisfy a certain system of differential equations, he defines by the introduction of new parameters μ a family of transformations E_μ,

$$x'_i = F_i(\bar{x}'_1, \ldots \bar{x}'_n, \mu_1, \ldots \mu_r)$$
$$(i = 1, 2 \ldots n),$$

each of which is generated by an infinitesimal transformation. Lie then establishes the symbolic equation

$$T_{\bar{a}} E_\mu = T_a, \ddagger$$

* Transformationsgruppen, III. 590; Continuierliche Gruppen, 211, 305, 390.

† Transformationsgruppen, III. 563; Continuierliche Gruppen, 376.

‡ If the equations defining the families of transformations T_a and E_μ are, respectively,

$$x'_i = f_i(x_1 \ldots x_n, a_1 \ldots a_r)$$
$$(i = 1, 2 \ldots n),$$

and

$$x'_i = F_i(\bar{x}'_1 \ldots \bar{x}'_n, \mu_1 \ldots \mu_r)$$
$$(i = 1, 2 \ldots n),$$

the symbolic equation $T_{\bar{a}} E_\mu = T_a$ is equivalent to the simultaneous system of equations

where the $\bar{a}$'s and μ's are arbitrary, and

$$a_k = \Phi_k(\mu_1 \dots \mu_r, \bar{a}_1 \dots \bar{a}_r)$$
$$(k = 1, 2 \dots r),$$

the Φ's being independent functions of the μ's. For

$$\bar{a}_k = a_k^{(0)}$$
$$(k = 1, 2 \dots r),$$

the transformation $T_{\bar{a}}$ becomes the identical transformation; and therefore we have

$$E_\mu = T_{a^{(0)}} E_\mu = T_a,\text{*}$$

where

$$a_k = \Phi_k(\mu_1 \dots \mu_r, a_1^{(0)} \dots a_r^{(0)})$$
$$(k = 1, 2 \dots r).$$

Thus every transformation of the family E_μ is a transformation of the family T_a. If, conversely, we could show that, for arbitrary values of the a's, every transformation T_a belonged to the family E_μ, it would follow that

$$T_{\bar{a}} T_a = T_a,\dagger$$

that is to say, we should then have shown that the family of transformations T_a forms a group.

But, although the Φ's are independent functions of the μ's, nevertheless the μ's in certain cases may be infinite for certain systems of values of the a's; and infinite values of the μ's, by their definition, are excluded

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$$\bar{x}'_i = f_i(x_1 \dots x_n, \bar{a}_1 \dots \bar{a}_r),$$
$$x'_i = F_i(\bar{x}'_1 \dots \bar{x}'_n, \mu_1 \dots \mu_r), \quad (i = 1, 2 \dots n),$$
$$x'_i = f_i(x_1 \dots x_n, a_1 \dots a_r),$$

or, to the functional equations

$$F_i(f_1(x, \bar{a}) \dots f_n(x, \bar{a}), \mu_1 \dots \mu_r) = f_i(x_1 \dots x_n, a_1 \dots a_r)$$
$$(i = 1, 2 \dots n).$$

* That is,

$$F_i(\bar{x}'_1 \dots \bar{x}'_n, \mu_1 \dots \mu_r) = F_i(f_1(x, a^{(0)}) \dots f_n(x, a^{(0)}), \mu_1 \dots \mu_r) = f_i(x_1 \dots x_n, a_1 \dots a_r)$$
$$(i = 1, 2 \dots n),$$

since

$$\bar{x}'_i = f_i(x_1 \dots x_n, a_1^{(0)} \dots a_r^{(0)})$$
$$(i = 1, 2 \dots n).$$

† That is

$$f_i(f_1(x, \bar{a}) \dots f_n(x, \bar{a}), a_1 \dots a_r) = f_i(x_1 \dots x_n, a_1 \dots a_r)$$
$$(i = 1, 2 \dots n).$$

at the outset.* We cannot then assume that every transformation T_a belongs to the family E_μ.

We may, however, proceed as follows: For all values of the a's for which the functions $\mu_j = M_j(a_1 \ldots a_r, a_1^{(0)} \ldots a_r^{(0)})$ $(j = 1, 2 \ldots r)$ are finite, we have

$$T_{\mathfrak{a}} T_a = T_{\mathfrak{a}} E_\mu = T_a,$$

that is,

$$f_i(f_1(x, \bar{a}) \ldots f_n(x, \bar{a}), a_1 \ldots a_r) = F_i(f_1(x, \bar{a}) \ldots f_n(x, \bar{a}), \mu_1 \ldots \mu_r)$$
$$= f_i(x_1 \ldots x_n, a_1 \ldots a_r)$$
$$(i = 1, 2 \ldots n).$$

Let $\beta_1, \beta_2 \ldots$ be a system of values of the a's for which one, or more, of the corresponding μ's is infinite. Also let $b_1, b_2 \ldots$ be the system of values assumed by the a's for $a_k = \beta_k$ $(k = 1, 2 \ldots r)$. Since the functions f are continuous functions of the variables and parameters, and since we assume that the system of parameters β give a definite transformation T_β of the family, we have

$$f_i(f_1(x, \bar{a}) \ldots f_n(x, \bar{a}), \beta_1 \ldots \beta_r)$$
$$= \lim_{a=\beta} f_i(f_1(x, \bar{a}) \ldots f_n(x, \bar{a}), a_1 \ldots a_r)$$
$$= \lim_{a=b} f_i(x_1 \ldots x_n, a_1 \ldots a_r) = f_i(x_1 \ldots x_n, b_1 \ldots b_r)$$
$$(i = 1, 2 \ldots n),$$

which is equivalent to the symbolic equation

$$T_{\mathfrak{a}} T_\beta = T_{\mathfrak{a}} \lim_{a=\beta} T_a = \lim_{a=\beta} T_{\mathfrak{a}} T_a = \lim_{a=b} T_a = T_b.$$

Consequently, the composition of two arbitrary transformations $T_{\mathfrak{a}}$ and T_β of the family is equivalent to a transformation T_b of this family; that is to say, the family of transformations T_a forms a group. The transformation T_b, however, may not be a transformation of the group that can be generated by an infinitesimal transformation of the group. Thus, every transformation of a group with continuous parameters and containing the identical transformation is not necessarily generated by an infinitesimal transformation of the group.†

Professors Study and Engel were the first to point this out, and thus establish a distinction between a group with continuous parameters and a continuous group. ‡ They found that not every transformation of the

* These Proceedings, XXXV. 247.

† These Proceedings, XXXV. 483–485.

‡ Engel: Leipziger Berichte, 1892.

special linear homogeneous group can be generated by an infinitesimal transformation of the group, and consequently this group is not properly continuous in the sense in which Lie uses the term. Since this important discovery, the subject of continuity has been investigated for the case of the general linear homogeneous group and its sub-groups, as well as for various other groups, by Professor Taber and his pupils, and from a geometrical standpoint by Professors Newson and Emch.*

This paper contains an investigation of the relation of the continuity of a group generated by infinitesimal transformations to its structure (*Zusammensetzung*), and the classification of all possible types of structure of complex groups with two, three, and four parameters with reference to the continuity of groups of these types. All possible types of groups with two, three, and four parameters can be divided into three classes. Every group is continuous whose structure is of a type belonging to the first class; every group is discontinuous whose structure is of a type drawn from the second class; and of the groups whose structure is of a type belonging to the third class, some are continuous and some are discontinuous. The parameter group of a given group G_r has the same structure as G_r; and every group of a given structure has the same parameter group. In every case which I have examined, the parameter group is discontinuous unless its type of structure is of the first class. I have considered not only complex groups, but also real groups generated by infinitesimal transformations.

§ 2.

The criterion for the continuity of an r-parameter group G_r is obtained as follows. Let $X_1 \ldots X_r$ be any system of independent infinitesimal transformations of G_r. The equations of G_r in their *canonical form* † are then

$$(1) \qquad x'_i = f_i(x_1 \ldots x_n, a_1 \ldots a_r) \qquad (i = 1, 2 \ldots n),$$

where $f_i(x, a)$, for $i = 1, 2 \ldots n$, is defined in the neighborhood of the identical transformation by the series

* Taber: Am. Jour. Maths., XVI.; Bull. Am. Math. Soc., July, 1894, April, 1896, Jan. 1897, Feb. 1900; Math. Ann., XLVI.; These Proceedings, XXXV. 577. Rettger: These Proceedings, XXXIII. 493–499; Am. Jour. Maths., XXII. Williams: These Proceedings, XXXV. 97–107. Newson: Kansas Univ. Quart., IV., V. 1896. Emch: Kansas Univ. Quart., IV., V. 1896.

† Transformationsgruppen, I. 171, III. 607; Continuierliche Gruppen, 454.

$$x_i + \sum_1^r{}_j a_j X_j x_i + \frac{1}{2!} \sum_1^r{}_j \sum_1^r{}_k a_j a_k X_j X_k x_i + \ldots$$

The transformation defined by equations (1) (the general transformation of this group) may be denoted by T_a. For finite values of the parameters $a_1, a_2 \ldots a_r$, the transformation T_a is generated by the infinitesimal transformation

$$a_1 X_1 + a_2 X_2 + \ldots + a_r X_r;$$

but for infinite values of $a_1, a_2 \ldots a_r$, T_a is not generated by an infinitesimal transformation of the group unless $T_a = T_{\alpha}$, the parameters $\alpha_1, \alpha_2 \ldots \alpha_r$ being all finite.* The transformation T_b is defined by

$$x''_i = f_i(x'_1 \ldots x'_n, b_1 \ldots b_r) \tag{2}$$
$$(i = 1, 2 \ldots n);$$

and the transformation $T_b T_a$, obtained by the composition of the transformations T_a and T_b,† is equivalent to a transformation T_c, defined by

$$x''_i = f_i(x_1 \ldots x_n, c_1 \ldots c_r) \tag{3}$$
$$(i = 1, 2 \ldots n),$$

where

$$c_k = \varphi_k(a_1 \ldots a_r, b_1 \ldots b_r) \tag{4}$$
$$(k = 1, 2 \ldots r).$$

If the c's can be taken finite for every finite system of values of the a's and b's, the group is continuous. If, however, it is possible to assign finite values to the a's and b's such that in each system of values of the c's one (or more) of the c's becomes infinite, the transformation $T_b T_a$ cannot be generated by an infinitesimal transformation of the group, and consequently the group is discontinuous.‡ A transformation which cannot be generated by an infinitesimal transformation of the group may be termed *essentially singular*.§ If the parameters a and b are taken sufficiently small, the transformation $T_b T_a$ can always be generated by an infinitesimal transformation, and, consequently, Lie's chief theorem holds in the neighborhood of the identical transformation.

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* Taber: These Proceedings, XXXV. 579.

† $T_b T_a$ will denote the transformation obtained by applying to the manifold $(x_1 \ldots x_n)$ first the transformation T_a and then the transformation T_b. Lie denotes this resultant transformation by $T_a T_b$.

‡ Cf. Rettger: Am. Jour. Maths., XXII.

§ Taber: Bull. Am. Math. Soc., VI. 199–203; These Proceedings, XXXV. 580.

If the system of equations (4) be written in the form

$$(5)\qquad a'_k = \phi_k(a_1 \ldots a_r, a_1 \ldots a_r) \qquad (k = 1, 2 \ldots r),$$

it can be shown that they define an r-parameter group in the variables a and a', with parameters $a_1 \ldots a_r$. That is to say, from

$$(5)\qquad a'_k = \phi_k(a_1 \ldots a_r, a_1 \ldots a_r) \qquad (k = 1, 2 \ldots r)$$

and

$$(6)\qquad a''_k = \phi_k(a'_1 \ldots a'_r, \beta_1 \ldots \beta_r) \qquad (k = 1, 2 \ldots r),$$

we have

$$(7)\qquad a''_k = \phi_k(a_1 \ldots a_r, \gamma_1 \ldots \gamma_r) \qquad (k = 1, 2 \ldots r),$$

where

$$(8)\qquad \gamma_j = \phi_j(a_1 \ldots a_r, \beta_1 \ldots \beta_r) \qquad (j = 1, 2 \ldots r).$$

The group thus defined is termed the *parameter group* of the group G_r.* Since the equations defining the transformations of the parameter group involve the functions ϕ, this group is especially important in the study of groups generated by infinitesimal transformations.

In general there is more than one system of functions ϕ such that

$$T_c = T_b T_a,$$

provided

$$c_j = \phi_j(a_1 \ldots a_r, b_1 \ldots b_r) \qquad (j = 1, 2 \ldots r).$$

But it may happen that the equations defining one group of a given structure restrict the functions c to fewer systems of values than in the case of another group of the same structure. Thus it is possible that of two groups of a given structure one shall be continuous and the other discontinuous.†

These statements are exemplified by a consideration of two groups $G_2^{(1)}$ and $G_2^{(2)}$, whose infinitesimal transformations are, respectively, p_1, $x_1 p_1$, and p_2, $x_2 p_2 + p_1$.‡ Both of these groups have the structure

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* Transformationsgruppen, I. 401 *et seq.*

† Cf. Bull. Am. Math. Soc., VI. 202.

‡ Throughout this paper Lie's notation will be followed, in accordance with which

$$p_1 \equiv \frac{\partial}{\partial x_1}, \quad p_2 \equiv \frac{\partial}{\partial x_2}, \quad \ldots \quad p_r \equiv \frac{\partial}{\partial x_r}.$$

$(X_1, X_2) \equiv X_1$. The canonical form of the finite equations of the group p_1, $x_1 p_1$ is

$$(9) \qquad \begin{aligned} x'_1 &= x_1 e^{a_2} + \frac{a_1}{a_2}(e^{a_2} - 1), \\ x'_2 &= x_2. \end{aligned}$$

These equations define the transformation T_a of $G_2^{(1)}$. Similarly, the equations defining the transformation T_b of $G_2^{(1)}$ are

$$(10) \qquad \begin{aligned} x''_1 &= x'_1 e^{b_2} + \frac{b_1}{b_2}(e^{b_2} - 1), \\ x''_2 &= x'_2. \end{aligned}$$

The transformation $T_b T_a$, obtained by the composition of the transformations T_a and T_b, is defined by

$$(11) \qquad \begin{aligned} x''_1 &= e^{a_2 + b_2} x_1 + \frac{a_1}{a_2}(e^{a_2} - 1)\, e^{b_2} + \frac{b_1}{b_2}(e^{b_2} - 1), \\ x''_2 &= x_2; \end{aligned}$$

and, if this is equivalent to a transformation T_c of the group, we have also

$$(12) \qquad \begin{aligned} x''_1 &= x_1 e^{c_2} + \frac{c_1}{c_2}(e^{c_2} - 1), \\ x''_2 &= x_2. \end{aligned}$$

Therefore

$$(13) \qquad \begin{aligned} c_1 &= \frac{a_2 + b_2 + 2\,k\,\pi\sqrt{-1}}{e^{a_2 + b_2} - 1}\left[e^{b_2}\frac{a_1}{a_2}(e^{a_2} - 1) + \frac{b_1}{b_2}(e^{b_2} - 1)\right] \\ &\equiv \phi_1(a_1, a_2, b_1, b_2), \\ c_2 &= a_2 + b_2 + 2\,k\,\pi\sqrt{-1}, \qquad \equiv \phi_2(a_1, a_2, b_1, b_2), \end{aligned}$$

where k is an arbitrary integer. Consequently for $G_2^{(1)}$ there is more than one system of functions ϕ. Provided $a_2 + b_2$ is not an even multiple of $\pi\sqrt{-1}$, every system of values of c_1 and c_2 is finite. For $a_2 + b_2 = 2\,\kappa\,\pi\sqrt{-1}$, c_2 is finite, but the denominator of c_1 becomes zero. In this case, however, that system of values of c_1 corresponding to $k = -\kappa$ is finite. Consequently the parameters c_1 and c_2 can always be chosen finite, and therefore $G_2^{(1)}$ is continuous.

For the group $G_2^{(2)}$, whose infinitesimal transformations are p_2, $x_2 p_2 + p_1$, T_a is defined by

$$(14) \qquad \begin{aligned} x'_1 &= x_1 + a_2, \\ x'_2 &= x_2 e^{a_2} + \frac{a_1}{a_2}(e^{a_2} - 1), \end{aligned}$$

and T_b by

$$
(15) \qquad \begin{aligned} x''_1 &= x'_1 + b_2, \\ x''_2 &= x'_2 e^{b_2} + \frac{b_1}{b_2}(e^{b_2} - 1). \end{aligned}
$$

Consequently the transformation $T_b\,T_a$ is defined by

$$
(16) \qquad \begin{aligned} x''_1 &= x_1 + a_2 + b_2, \\ x''_2 &= x_2 e^{a_2 + b_2} + e^{b_2}\frac{a_1}{a_2}(e^{a_2} - 1) + \frac{b_1}{b_2}(e^{b_2} - 1), \end{aligned}
$$

whence, if $T_b\,T_a = T_c$,

$$
(17) \qquad \begin{aligned} c_1 &= \frac{a_2 + b_2}{e^{a_2 + b_2} - 1}\left[e^{b_2}\frac{a_1}{a_2}(e^{a_2} - 1) + \frac{b_1}{b_2}(e^{b_2} - 1)\right] \equiv \phi_1(a_1, a_2, b_1, b_2), \\ c_2 &= a_2 + b_2. \qquad \equiv \phi_2(a_1, a_2, b_1, b_2). \end{aligned}
$$

In this case there is but one system of functions ϕ. If, now, $a_2 + b_2$ is an even multiple of $\pi\sqrt{-1}$, c_2 is finite, but c_1 is infinite; that is, there is no finite parameter c_1 corresponding to this choice of the parameters a and b. Consequently, if $a_2 + b_2 = 2\,k\,\pi\sqrt{-1} \neq 0$, $T_b\,T_a$ cannot be generated by an infinitesimal transformation of the group, and therefore $G_2^{(2)}$ is discontinuous.*

Lie states that two groups having the same structure are (holohedrically) isomorphic; but the groups $G_2^{(1)}$ and $G_2^{(2)}$ are not properly isomorphic, except in the neighborhood of the identical transformation, since one is continuous and the other discontinuous. Whence it appears that the conception of isomorphism, as developed by Lie, requires modification.

The parameter group of $G_2^{(1)}$ is defined by the equations

$$
(13\text{ a}) \qquad \begin{aligned} a'_1 &= \frac{a_2 + a_2 + 2\,k\,\pi\sqrt{-1}}{e^{a_2 + a_2} - 1}\left[e^{a_2}\frac{a_1}{a_2}(e^{a_2} - 1) + \frac{a_1}{a_2}(e^{a_2} - 1)\right], \\ a'_2 &= a_2 + a_2 + 2\,k\,\pi\sqrt{-1}, \end{aligned}
$$

* For the group $\frac{x_2 p_1}{2}$, $\frac{1}{2}(x_1 p_1 - x_2 p_2)$, which also has the structure $(X_1, X_2) \equiv X_1$, we have

$$
\begin{aligned} c_1 &= \frac{a_2 + b_2 + 4\,k\,\pi\sqrt{-1}}{e^{a_2 + b_2} - 1}\left[e^{b_2}\frac{a_1}{a_2}(e^{a_2} - 1) + \frac{b_1}{b_2}(e^{b_2} - 1)\right] \equiv \phi_1(a_1, a_2, b_1, b_2), \\ c_2 &= a_2 + b_2 + 4\,k\,\pi\sqrt{-1}; \qquad \equiv \phi_2(a_1, a_2, b_1, b_2), \end{aligned}
$$

and if $a_2 + b_2 = 2(2\kappa + 1)\pi\sqrt{-1}$, where κ is an integer, c_1 is always infinite. Consequently this group is also discontinuous.

where k is any integer, and of $G_2^{(2)}$ by the equations

$$(17\text{ a})\qquad \begin{aligned} a'_1 &= \frac{a_2 + a_2}{e^{a_2 + a_2} - 1}\left[e^{a_2}\frac{a_1}{a_2}(e^{a_2} - 1) + \frac{a_1}{a_2}(e^{a_2} - 1)\right], \\ a'_2 &= a_2 + a_2. \end{aligned}$$

Nevertheless, for any value of k, the parameter group of $G_2^{(1)}$ is identical with the parameter group of $G_2^{(2)}$. For let $S_a^{(1)}$ denote the transformation defined by equations (13 a), and $S_a^{(2)}$ the transformation defined by equations (17 a). Then for any system of values of a_1, a_2, and for any value of k, we have, by properly choosing β_1, β_2,

$$S_a^{(1)} = S_\beta^{(2)};$$

which symbolic equation persists for β_1, β_2, and k arbitrary, if a_1, a_2 are properly chosen.*

Let T_a be an arbitrary transformation of G_r, defined by the equations

$$x'_i = x_i + \sum_1^r{}_j a_j X_j x_i + \frac{1}{2!}\sum_1^r{}_j \sum_1^r{}_k a_j a_k X_j X_k x_i + \ldots$$
$$(i = 1, 2 \ldots n).$$

The transformation T_a^{-1}, inverse to T_a, is then defined by the equations which we obtain on replacing $a_1, a_2 \ldots$ by their negatives.† Compound the transformation T_a and its inverse with each transformation T_a of G_r so as to obtain the transformation $T_a T_a T_a^{-1}$, which is also a transformation of G_r; and let

$$(18)\qquad T_{a'} = T_a T_a T_a^{-1}.\ddagger$$

Let

$$(19)\qquad T_{a''} = T_\beta T_{a'} T_\beta^{-1}.$$

Then, if

$$(20)\qquad T_\gamma = T_\beta T_a,$$

we have

$$(21)\qquad T_{a''} = T_\gamma T_a T_\gamma^{-1}.$$

---

* Equations (13 a) may be regarded as defining a group with three parameters a_1, a_2, and k, of which two, a_1 and a_2, vary continuously, and one, namely k, takes only integer values. But this group is not a mixed group, since we have shown that k is unessential, that is, it is immaterial what value is assigned to k.

† Transformationsgruppen, I. 52, 53.

‡ The transformation $T_{a'}$ is said by Lie to be obtained by the application (*Ausführung*) of T_a to the transformations T_a of G_r. Cf. Lie: Continuierliche Gruppen, 445 *et seq.*

The symbolic equation (18) may be regarded as defining a transformation between the parameters a and a' of G_r, and is equivalent to r equations of the form

$$a'_j = F_j(a_1 \ldots a_r, a_1 \ldots a_r) \qquad (j = 1, 2 \ldots r). \tag{22}$$

Similarly, (19) is equivalent to

$$a''_j = F_j(a'_1 \ldots a'_r, \beta_1 \ldots \beta_r) \qquad (j = 1, 2 \ldots r),$$

and (21) to

$$a''_j = F_j(a_1 \ldots a_r, \gamma_1 \ldots \gamma_r) \qquad (j = 1, 2 \ldots r),$$

and, in virtue of (20),

$$\gamma_j = \phi_j(a_1 \ldots a_r, \beta_1 \ldots \beta_r) \qquad (j = 1, 2 \ldots r).$$

Thus equations (22) define a group Γ, which is termed the *adjoined* of G_r.* The number of variables of the group Γ is r, and it contains r parameters, but these are not necessarily all essential. The number of essential parameters in Γ is less than r by one for each independent infinitesimal transformation of G_r commutative with each of the infinitesimal transformations $X_1 \ldots X_r$.† Thus, if G_r contains just s such independent infinitesimal transformations, Γ is an $(r - s)$-parameter group.

The canonical form of the equations defining the transformation T_a of $G_2^{(1)}$ is

$$\text{(9 a)} \qquad x'_1 = x_1 e^{a_2} + \frac{a_1}{a_2}(e^{a_2} - 1), \qquad x'_2 = x_2,$$

and consequently, if $T_{a'} = T_\alpha T_a T_\alpha^{-1}$, we have

$$\text{(23)} \qquad \begin{aligned} a'_1 &= \frac{a_2 + 2k\pi\sqrt{-1}}{a_2} a_1 e^{-a_2} - (a_2 + 2k\pi\sqrt{-1})\frac{a_1}{a_2}(e^{-a_2} - 1) \equiv F_1(a_1, a_2, a_1, a_2), \\ a'_2 &= a_2 + 2k\pi\sqrt{-1} \equiv F_2(a_1, a_2, a_1, a_2), \end{aligned}$$

where k is an arbitrary integer. The family of transformations between the variables a and a' which we obtain for any assigned integer value of

* Transformationsgruppen, I. 272, 275; III. 667–670. Continuierliche Gruppen, 454–455.

† Transformationsgruppen, I. 277.

k interchanges the transformations of $G_2^{(1)}$ (so that T_a becomes $T_{a'}$), but this family of transformations does not form a group, except for $k = 0$; in which case it is the adjoined of $G_2^{(1)}$. This adjoined group, $\Gamma^{(1)}$, is generated by the infinitesimal transformations

$$-a_2 \frac{\partial}{\partial a_1}, \quad a_1 \frac{\partial}{\partial a_1}.$$

We may regard a_1, a_2, and k as parameters, a_1, a_2 varying continuously, and k taking only integer values, and then we have a family of transformations (interchanging the transformations of $G_2^{(1)}$) that forms a mixed group, of which $\Gamma^{(1)}$ is a sub-group. Only those transformations of this mixed group which belong to $\Gamma^{(1)}$ are generated by an infinitesimal transformation of this mixed group. This mixed group might be called the adjoined of $G_2^{(1)}$, in which case the adjoined of a given group G_r would appear as a mixed group containing more than r parameters, some of which, however, do not vary continuously.

In the case of the group $G_2^{(2)}$ the transformation T_a is defined by the equations

$$\text{(14 a)} \qquad \begin{aligned} x'_1 &= x_1 + a_2, \\ x'_2 &= x_2 e^{a_2} + \frac{a_1}{a_2}(e^{a_2} - 1), \end{aligned}$$

and if $T_{a'} = T_\alpha T_a T_\alpha^{-1}$, we have

$$\text{(24)} \qquad \begin{aligned} a'_1 &= a_1 e^{-\alpha_2} - a_2 \frac{\alpha_1}{\alpha_2}(e^{-\alpha_2} - 1) \equiv F_1(a_1, a_2, \alpha_1, \alpha_2), \\ a'_2 &= a_2 \qquad\qquad\qquad\qquad\qquad\quad \equiv F_2(a_1, a_2, \alpha_1, \alpha_2). \end{aligned}$$

Consequently the adjoined of the group $G_2^{(2)}$ cannot be regarded as a mixed group. Thus the equations of the adjoined, obtained from the symbolic equation $T_{a'} = T_\alpha T_a T_\alpha^{-1}$, are not necessarily all linear and homogeneous. However, they will always include one system of linear homogeneous equations that define a family of transformations generated by infinitesimal transformations, and forming a group.

Lie has shown that if $X_1 \ldots X_r$ generate an r-parameter group G_r in the n variables $x_1 \ldots x_n$, and subject to the conditions

$$(X_j, X_k) \equiv \sum_1^r{}_s\, c_{jks} X_s$$
$$(j, k = 1, 2 \ldots r),$$

the c's being the structural constants, the adjoined group is generated by the infinitesimal transformations

$$E_\nu \equiv \sum_1^r{}_k \sum_1^r{}_\mu c_{\mu\nu k}\, a_\mu \frac{\partial}{\partial a_k}$$
$$(\nu = 1, 2 \ldots r),$$

and $E_1 \ldots E_r$ satisfy the conditions

$$(E_j, E_k) \equiv \sum_1^r{}_s c_{jks} E_s$$
$$(j, k = 1, 2 \ldots r).*$$

The infinitesimal transformations $E_1 \ldots E_r$, however, are not necessarily all independent. The number of independent infinitesimal transformations of the adjoined of G_r will be one less for each infinitesimal transformation of G_r that is commutative with every infinitesimal transformation of G_r (*ausgezeichnete Transformation*), as mentioned above, page 95. Such a transformation will be called an extraordinary transformation of G_r. It follows, from what has been said, that every group of the same structure has the same adjoined. If G_r contains no extraordinary transformation, G_r and Γ have the same structure. If Γ contains an essentially singular transformation, G_r must also contain at least one essentially singular transformation. Therefore, if Γ is discontinuous, every group of which Γ is the adjoined is discontinuous.† But Γ is not necessarily discontinuous if G_r contains an essentially singular transformation.

By Lie's theorem,‡ the infinitesimal transformations of the adjoined of $G_2^{(1)}$ and also of $G_2^{(2)}$ (since both have the same structure) are

$$-a_2 \frac{\partial}{\partial a_1}, \quad a_1 \frac{\partial}{\partial a_1},$$

and thus the finite equations of the adjoined are

$$(25) \qquad \begin{aligned} a'_1 &= a_1 e^{a_2} - a_2 \frac{\alpha_1}{\alpha_2}(e^{\alpha_2} - 1), \\ a'_2 &= a_2, \end{aligned}$$

which result agrees with the equations deduced page 95.

§ 3.

In what follows I shall denote by α, β, γ, respectively, the following differential operators:

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* Transformationsgruppen, I. 275; Continuierliche Gruppen, pp. 466–467.

† Taber: Bull. Am. Math. Soc., VI. 203; These Proceedings, XXXV. 590.

‡ Cf. Continuierliche Gruppen, p. 467.

$$\alpha = a_1 X_1 + a_2 X_2 + \ldots + a_r X_r,$$
$$\beta = b_1 X_1 + b_2 X_2 + \ldots + b_r X_r,$$
$$\gamma = c_1 X_1 + c_2 X_2 + \ldots + c_r X_r,$$

where the a's, b's, and c's denote arbitrary parameters, and by e^α the operator

$$(1 + \alpha + \frac{\alpha^2}{2!} + \frac{\alpha^3}{3!} + \ldots) f \equiv f + \alpha f + \frac{\alpha^2}{2!} f + \frac{\alpha^3}{3!} f + \ldots,$$

where $\alpha^{m+1} f \equiv \alpha (\alpha^m f)$.

Let

$$X = \sum_1^n {}_i\, \xi_i (x) \frac{\partial}{\partial x_i},$$

and let

$$x'_i = x_i + t X x_i + \frac{t^2}{2!} X^2 x_i + \frac{t^3}{3!} X^3 x_i + \ldots = e^{tX} x_i$$
$$(i = 1, 2 \ldots n).$$

Since the x''s are functions of t, any function of the x''s, $f(x'_1 \ldots x'_n)$, is also a function of t. And we have

$$f(x'_1 \ldots x'_n)$$
$$= [f(x')]_{t=0} + t \left[\frac{df(x')}{dt}\right]_{t=0} + \frac{t^2}{2!}\left[\frac{d^2 f(x')}{dt^2}\right]_{t=0} + \frac{t^3}{3!}\left[\frac{d^3 f(x')}{dt^3}\right]_{t=0} + \ldots$$
$$(i = 1, 2 \ldots n).$$

But

$$\frac{df(x')}{dt} = \sum_1^n {}_i \frac{\partial f(x')}{\partial x'_i} \frac{dx'_i}{dt} = \sum_1^n {}_i\, \xi_i (x') \frac{\partial f(x')}{\partial x'_i} = X' f(x'),$$

where X' denotes the result of substituting the accented for the unaccented variables in X. Therefore

$$f(x'_1 \ldots x'_n)$$
$$= [f(x')]_{t=0} + t [X' f(x')]_{t=0} + \frac{t^2}{2!} [X'^2 f(x')]_{t=0} + \frac{t^3}{3!} [X'^3 f(x')]_{t=0} + \ldots$$
$$= f(x) + t X f(x) + \frac{t^2}{2!} X^2 f(x) + \frac{t^3}{3!} X^3 f(x) + \ldots$$
$$= e^{tX} f(x_1 \ldots x_n).$$

Consequently, if

$$x'_i = e^\alpha x_i$$
$$(i = 1, 2 \ldots n),$$

we have

$$f_i (x'_1 \ldots x'_n) = e^\alpha f_i (x_1 \ldots x_n)$$
$$(i = 1, 2 \ldots n).$$

Let now

$$x'_i = f_i(x_1 \ldots x_n, a_1 \ldots a_r) = e^{\alpha} x_i$$
$$(i = 1, 2 \ldots n),$$

and

$$x''_i = f_i(x'_1 \ldots x'_n, b_1 \ldots b_r) = e^{\beta'} x'_i$$
$$(i = 1, 2 \ldots n),$$

where β' denotes the result of substituting the accented for the unaccented variables in the X's which appear in the operator β. Then, by what precedes, we have

$$\begin{aligned} x''_i &= f_i(x'_1 \ldots x'_n, b_1 \ldots b_r) \\ &= e^{\alpha} f_i(x_1 \ldots x_n, b_1 \ldots b_r) = e^{\alpha}(e^{\beta} x_i) \end{aligned}$$
$$(i = 1, 2 \ldots n).$$

Let the operator $e^{\alpha} e^{\beta}$ be defined as follows:

$$(e^{\alpha} e^{\beta}) f$$
$$= \left(1 + (\alpha + \beta) + \frac{1}{2!}(\alpha^2 + 2\alpha\beta + \beta^2) + \frac{1}{3!}(\alpha^3 + 3\alpha^2\beta + 3\alpha\beta^2 + \beta^3) + \ldots\right) f$$
$$= f + (\alpha + \beta) f + \frac{1}{2!}(\alpha^2 + 2\alpha\beta + \beta^2) f + \frac{1}{3!}(\alpha^3 + 3\alpha^2\beta + 3\alpha\beta^2 + \beta^3) f + \ldots$$

Then

$$(e^{\alpha} e^{\beta}) x_i = e^{\alpha}(e^{\beta} x_i)$$
$$(i = 1, 2 \ldots n),$$

and therefore

$$x''_i = (e^{\alpha} e^{\beta}) x_i$$
$$(i = 1, 2 \ldots n);$$

thus $e^{\alpha} e^{\beta}$ denotes the result of the composition in the order named of the transformations denoted by e^{α} and e^{β}.*

By § 2, page 94, the transformation inverse to e^{α} is $e^{-\alpha}$. Let δt denote an infinitesimal constant. Since the transformation $e^{\alpha + \delta t \gamma}$ is infinitely near the transformation e^{α}, the transformation $e^{-\alpha} e^{\alpha + \delta t \gamma}$ is an infinitesimal transformation. If we denote its parameters by $\delta t b_1$, $\delta t b_2 \ldots \delta t b_r$, we have

$$e^{-\alpha} e^{\alpha + \delta t \gamma}$$
$$= 1 + \delta t \{\gamma - \frac{1}{2!}(\alpha, \gamma) + \frac{1}{3!}(\alpha, (\alpha, \gamma)) - \frac{1}{4!}(\alpha, (\alpha, (\alpha, \gamma))) + \ldots\} + \ldots$$
$$= e^{\delta t \beta} = 1 + \delta t \beta + \ldots$$

in which (α, γ) denotes the alternant $\alpha\gamma - \gamma\alpha$; and neglecting infinitesimals of the second and higher orders, we have

$$(26) \quad \beta = \gamma - \frac{1}{2!}(\alpha, \gamma) + \frac{1}{3!}(\alpha, (\alpha, \gamma)) - \frac{1}{4!}(\alpha, (\alpha, (\alpha, \gamma))) + \ldots$$

* Cf. Campbell: Proc. London Math. Soc., XXVIII. 381–390. Also Poincaré: Comptes Rendus, Mai 1er, 1899.

By supposition $\gamma = \sum_1^r{}_j c_j X_j$; and since the r infinitesimal transformations $X_1 \ldots X_r$ satisfy the Lieschen criterion,

$$(a, \gamma) = (\sum_1^r{}_j a_j X_j, \sum_1^r{}_k c_k X_k) = \sum_1^r{}_j[(a_1 c_2 - a_2 c_1) c_{12j} + (a_1 c_3 - a_3 c_1) c_{13j} + \ldots] X_j.$$

Whence it follows that $(a, (a, \gamma))$, etc., are linear in $X_1 \ldots X_r$. It is to be observed that each term in the right member of (26) is linear in $c_1 \ldots c_r$. Since $X_1 \ldots X_r$ are independent, the coefficients of corresponding X's in the two members of (26) are equal. Therefore

$$(27)\qquad \begin{aligned} b_1 &= G_{11} c_1 + G_{12} c_2 + \ldots + G_{1r} c_r, \\ b_2 &= G_{21} c_1 + G_{22} c_2 + \ldots + G_{2r} c_r, \\ &\ldots\ldots\ldots\ldots\ldots \\ b_r &= G_{r1} c_1 + G_{r2} c_2 + \ldots + G_{rr} c_r, \end{aligned}$$

in which the G's are integral functions of $a_1 \ldots a_r$.*

Let the determinant of the G's be denoted by Δ, that is, let

$$\Delta \equiv \begin{vmatrix} G_{11}, & G_{12} & \ldots & G_{1r} \\ G_{21}, & G_{22} & \ldots & G_{2r} \\ \ldots & \ldots & \ldots & \ldots \\ G_{r1}, & G_{r2} & \ldots & G_{rr} \end{vmatrix}$$

The symbolic equation

$$e^{-a} e^{a + \delta t \gamma} = e^{\delta t \beta}$$

may be written

$$e^{a} e^{\delta t \beta} = e^{a + \delta t \gamma}.$$

If $\Delta \neq 0$ we may take $b_1 \ldots b_r$ arbitrarily, and by means of equations (27) determine the c's to satisfy this symbolic equation; in which case

$$(28)\qquad \begin{aligned} c_1 &= \frac{A_{11}}{\Delta} b_1 + \frac{A_{12}}{\Delta} b_2 + \ldots + \frac{A_{1r}}{\Delta} b_r, \\ c_2 &= \frac{A_{21}}{\Delta} b_1 + \frac{A_{22}}{\Delta} b_2 + \ldots + \frac{A_{2r}}{\Delta} b_r, \\ &\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ c_r &= \frac{A_{r1}}{\Delta} b_1 + \frac{A_{r2}}{\Delta} b_2 + \ldots + \frac{A_{rr}}{\Delta} b_r, \end{aligned}$$

* Schur and Engel. See Transformationsgruppen, III. 754 *et seq.* and 788 *et seq* See also These Proceedings, XXXV. 584, 585.

where $A_{\mu\nu}$ is the first minor of Δ relative to $G_{\nu\mu}$, and thus the A's are integral functions of $a_1, a_2 \ldots a_r$. Consequently, if $\Delta \neq 0$, the composition of the transformation e^{a} and an arbitrary infinitesimal transformation $e^{\delta t\beta}$ gives a transformation $e^{a+\delta t\gamma}$, infinitely near the transformation e^{a}, and generated by an infinitesimal transformation. Let $e^{a+\delta t\gamma}$ be denoted by e^{a_1}, that is, let $e^{a_1} = e^{a+\delta t\gamma}$, where

$$a_1 = a + \delta t \gamma = a_1^{(1)} X_1 + a_2^{(1)} X_2 + \ldots + a_r^{(1)} X_r.$$

Applying the infinitesimal transformation $e^{\delta t\beta}$ repeatedly, we thus obtain the equations

$$\begin{aligned} e^{a_1} &= e^{a} e^{\delta t\beta}, \\ e^{a_2} &= e^{a_1} e^{\delta t\beta} = e^{a} e^{2\delta t\beta}, \\ e^{a_3} &= e^{a_2} e^{\delta t\beta} = e^{a} e^{3\delta t\beta}, \\ &\ldots\ldots\ldots\ldots \\ e^{a_n} &= e^{a_{n-1}} e^{\delta t\beta} = e^{a} e^{n\delta t\beta}. \end{aligned}$$

For n infinite, $n\delta t$ is finite, and may be taken equal to unity; thus

$$e^{a_n} = e^{a} e^{\beta}.$$

Consequently, if Δ does not vanish for any system of values of $a_1 \ldots a_r$, in which case Δ is a constant,* then the composition of an arbitrary transformation e^{a} with finite parameters with an arbitrary transformation $e^{n\delta t\beta} = e^{\beta}$ with finite parameters, gives a transformation of the group with finite parameters which is generated by an infinitesimal transformation.

The form of Δ depends only on the structural constants, and thus Δ is the same for all groups of the same structure. Therefore, if the Δ corresponding to a given structure is a constant, the composition of two arbitrary transformations of any group of this structure gives a transformation of the group with finite parameters, that is, a non-singular transformation of the group, and consequently every group of this structure is continuous.†

If the Δ corresponding to a given structure vanishes for certain systems of values of $a_1 \ldots a_r$, some groups of this structure may be continuous and others discontinuous. For example, the two groups $G_2^{(1)}$ and $G_2^{(2)}$, considered above, page 92, both have the structure $(X_1, X_2) \equiv X_1$. The

* For complex groups Δ is either unity, or else vanishes for certain systems of values of $a_1 \ldots a_r$. See the expression for Δ as a product on page 104.

† This criterion of continuity is due to Professor Taber.

determinant Δ corresponding to this structure is $\Delta = \frac{e^{a_2} - 1}{a_2}$, and this vanishes for a_2 an even multiple, not zero, of $\pi\sqrt{-1}$. Nevertheless the group $G_2^{(1)}$ is continuous, whereas the group $G_2^{(2)}$ is discontinuous.

The symbolic equation $e^{a_1} = e^{a + \delta t \gamma}$ is equivalent to the system of equations

$$a_k^{(1)} = a_k + \delta t c_k$$
$$(k = 1, 2 \ldots r),$$

which define the infinitesimal transformation of the parameter group. But the infinitesimal transformation of the parameter group is defined by the equations

$$a_k^{(1)} = a_k + \sum_1^r {}_j \xi_{kj}(a) b_j \delta t$$
$$(k = 1, 2 \ldots r).*$$

Thereforo

$$c_k = \sum_1^r {}_j \xi_{kj}(a) b_j$$
$$(k = 1, 2 \ldots r).$$

If $\Delta \neq 0$, equations (28) give

$$c_k = \sum_1^r {}_j \frac{A_{kj}}{\Delta} b_j$$
$$(k = 1, 2 \ldots r).$$

Therefore, if $\mathfrak{A}_1 \ldots \mathfrak{A}_r$ denote the symbols of infinitesimal transformation of the parameter group, we have

$$\mathfrak{A}_j = \sum_1^r {}_k \xi_{jk}(a) \frac{\partial}{\partial a_k} = \sum_1^r {}_k \frac{A_{jk}}{\Delta} \frac{\partial}{\partial a_k}$$
$$(j = 1, 2 \ldots r).\dagger$$

To illustrate what precedes, consider the two-parameter structure

$$(X_1, X_2) \equiv X_1.$$

Equation (26) gives

$$b_1 X_1 + b_2 X_2 = c_1 X_1 + c_2 X_2 - \frac{1}{2!}(a_1 c_2 - a_2 c_1) X_1 - \frac{a_2}{3!}(a_1 c_2 - a_2 c_1) X_1$$
$$- \frac{a_2^2}{4!}(a_1 c_2 - a_2 c_1) X_1 - \frac{a_2^3}{5!}(a_1 c_2 - a_2 c_1) X_1 - \ldots$$

whence follows

$$(29) \qquad b_1 = \frac{e^{a_2} - 1}{a_2} c_1 - \frac{a_1}{a_2^2}(e^{a_2} - a_2 - 1) c_2,$$
$$b_2 = c_2.$$

---

* Transformationsgruppen, I. 55, 65.

† Engel and Schur, Transformationsgruppen, III. 754 *et seq.* and 788 *et seq.*

Consequently

$$\Delta = \begin{vmatrix} \dfrac{e^{a_2}-1}{a_2}, & -\dfrac{a_1}{a_2^2}(e^{a_2}-a_2-1) \\ 0, & 1 \end{vmatrix}$$

For a_2 an even multiple, not zero, of $\pi\sqrt{-1}$, Δ vanishes. Thus it is possible that some group of the above structure shall be discontinuous.

Equations (29) give

$$\text{(30)} \quad \begin{aligned} c_1 &= \frac{a_2}{e^{a_2}-1}\left[b_1 + \frac{a_1}{a_2^2}(e^{a_2}-a_2-1)b_2\right] \equiv \sum_1^r{}_j\, \xi_{1j}(a)\, b_j, \\ c_2 &= b_2 \qquad\qquad\qquad\qquad\qquad\qquad\qquad \equiv \sum_1^r{}_j\, \xi_{2j}(a)\, b_j. \end{aligned}$$

Therefore the infinitesimal transformations of the parameter group are

$$\mathfrak{A}_1 \equiv \frac{a_2}{e^{a_2}-1}\frac{\partial}{\partial a_1}.$$

$$\mathfrak{A}_2 \equiv \frac{a_1(e^{a_2}-a_2-1)}{a_2(e^{a_2}-1)}\frac{\partial}{\partial a_1} + \frac{\partial}{\partial a_2}.$$

As a second example, take the three-parameter structure

$$(X_1, X_2) \equiv 0, \quad (X_1, X_3) \equiv 0, \quad (X_2, X_3) \equiv X_1.$$

Equation (26) gives

$$b_1 X_1 + b_2 X_2 + b_3 X_3 = c_1 X_1 + c_2 X_2 + c_3 X_3 - \tfrac{1}{2}(a_2 c_3 - a_3 c_2) X_1.$$

Therefore

$$\text{(31)} \quad \begin{aligned} b_1 &= c_1 + \frac{a_3}{2}c_2 - \frac{a_2}{2}c_3, \\ b_2 &= c_2, \\ b_3 &= c_3; \end{aligned}$$

and

$$\Delta = \begin{vmatrix} 1, & \dfrac{a_3}{2}, & -\dfrac{a_2}{2} \\ 0, & 1, & 0 \\ 0, & 0, & 1 \end{vmatrix} = 1.$$

Whence it follows that all groups of the above structure are continuous.

Equations (31) give

$$
(32) \qquad
\begin{aligned}
c_1 &= b_1 - \frac{a_3}{2} b_2 + \frac{a_2}{2} b_3 &&\equiv \sum_1^r{}_j\, \xi_{1j}(a)\, b_j,\\
c_2 &= b_2 &&\equiv \sum_1^r{}_j\, \xi_{2j}(a)\, b_j,\\
c_3 &= b_3 &&\equiv \sum_1^r{}_j\, \xi_{3j}(a)\, b_j.
\end{aligned}
$$

Therefore, the infinitesimal transformations of the parameter group are

$$
\begin{aligned}
\mathfrak{A}_1 &\equiv \frac{\partial}{\partial a_1},\\
\mathfrak{A}_2 &\equiv -\frac{a_3}{2}\frac{\partial}{\partial a_1} + \frac{\partial}{\partial a_2},\\
\mathfrak{A}_3 &\equiv \frac{a_2}{2}\frac{\partial}{\partial a_1} + \frac{\partial}{\partial a_3}.
\end{aligned}
$$

By means of the methods explained above, I have examined the determinant Δ, and the adjoined group, corresponding to all possible types of structure of two-, three-, and four-parameter complex groups,* and the results are summarized in the table on pages 591–597, Vol. XXXV. of These Proceedings. For all types considered, the several elements (α, γ), $(\alpha, (\alpha, \gamma))$, etc., of (26) were calculated, and the Δ determined by the actual summation of the resulting series. Since making these calculations, Professor Taber has discovered a method of obtaining Δ immediately from (α, γ); † namely, we have

$$
(\alpha, \gamma) = \sum_1{}_j \left(\begin{vmatrix} a_1, & c_1 \\ a_2, & c_2 \end{vmatrix} c_{12j} + \begin{vmatrix} a_1, & c_1 \\ a_3, & c_3 \end{vmatrix} c_{13j} + \ldots \right) X_j.
$$

Let, now, ϕ denote the matrix

$$
\begin{pmatrix}
-\Sigma a_j c_{j11}, & -\Sigma a_j c_{j21} & \ldots & -\Sigma_j a_j c_{jr1} \\
-\Sigma a_j c_{j12}, & -\Sigma a_j c_{j22} & \ldots & -\Sigma_j a_j c_{jr2} \\
\ldots & \ldots & \ldots & \ldots \\
-\Sigma a_j c_{j1r}, & -\Sigma a_j c_{j2r} & \ldots & -\Sigma_j a_j c_{jrr}
\end{pmatrix}
$$

Then Δ is the determinant of the matrix $\dfrac{e^{\phi} - 1}{\phi}$; that is, if $\rho_1 \ldots \rho_r$ are the roots of the characteristic equation of ϕ, $\Delta = \prod_1^r{}_j \left(\dfrac{e^{\rho_j} - 1}{\rho_j}\right)$. The

* These structures are enumerated by Lie on pp. 565, 571, 574–589, Continuierliche Gruppen; and also on pp. 713, 716, 723–730, Transformationsgruppen, III.

† This method had previously been given by Professor Engel. See Transformationsgruppen, III. 788.

constituents of Δ are integral functions of the constituents of ϕ, and therefore integral functions of $a_1 \ldots a_r$.*

In every case for which the determinant Δ vanishes for certain systems of values of $a_1 \ldots a_r$, I have found at least one group of the corresponding structure which is discontinuous.

I have also determined the infinitesimal transformations which generate the parameter group corresponding to each structure enumerated in the above mentioned table; but since the symbols are in many cases very complicated, and are of no especial interest in themselves, I have not given them.

§ 4.

In this section let the variables and parameters be restricted to real values. We will then consider the continuity of real groups, that is, groups all of whose transformations are real.

Let
$$x'_i = f_i(x_1 \ldots x_n, a_1 \ldots a_r)$$
$$(i = 1, 2 \ldots n),$$

in which the f's are analytic functions of their arguments, define an r-parameter group of real transformations. Lie's chief theorem then states that r real, linearly independent, infinitesimal transformations

$$X_j \equiv \sum_1^n {}_k\, \xi_{jk}(x) \frac{\partial}{\partial x_k}$$
$$(j = 1, 2 \ldots r)$$

in the n real variables $x_1 \ldots x_n$, generate an r-parameter real group G_r if and only if $X_1 \ldots X_r$ satisfy the conditions

$$(X_j, X_k) \equiv \sum_1^r {}_s\, c_{jks} X_s$$
$$(j, k = 1, 2 \ldots r),$$

where the c_{jks} are real quantities independent of the X's.†

Since the structural constants c_{jks} must be real, there are more types of structure possible for real groups than for complex groups. For example, for the three-parameter structures

$$(X_1, X_2) \equiv X_1, \; (X_1, X_3) \equiv 2X_2, \; (X_2, X_3) \equiv X_3,$$

and

$$(X_1, X_2) \equiv -2X_1, \; (X_1, X_3) \equiv X_2, \; (X_2, X_3) \equiv -2X_3,$$

* Taber: These Proceedings, XXXV. 581.

† Transformationsgruppen, III. 360 *et seq.*

the structural constants c_{jks} are real, and one of these structures can be transformed into the other, but only by means of an imaginary transformation; consequently these structures are distinct for real groups.

The only possible types of structure of real or complex two-parameter groups are $(X_1, X_2) \equiv X_1$, and $(X_1, X_2) \equiv 0$. For the structure $(X_1, X_2) \equiv X_1$, $\Delta = \dfrac{e^{a_2} - 1}{a_2}$, which does not vanish for any real system of values of a_1, a_2; consequently all real groups of this structure are continuous. For the structure $(X_1, X_2) \equiv 0$, $\Delta = 1$; consequently all real and complex groups of this structure are continuous. Therefore all two-parameter real groups are continuous.

However, there exist three-parameter real groups which are discontinuous. Thus, let

$$(X_1, X_2) \equiv 0, \quad (X_1, X_3) \equiv X_2, \quad (X_2, X_3) \equiv - X_1.$$

For this structure we have

$$\Delta = \frac{e^{a_3\sqrt{-1}} - 1}{a_3\sqrt{-1}} \cdot \frac{e^{-a_3\sqrt{-1}} - 1}{- a_3\sqrt{-1}},$$

and Δ vanishes for real values of a_3, namely, when a_3 is an even multiple, not zero, of π. This indicates the possibility that discontinuous real groups of this structure may exist. The theorem in relation to the adjoined group, given in § 2, holds true also for real groups; namely, if the adjoined of a given real group G_r is discontinuous, G_r itself, and all groups having the same structure as G_r, are discontinuous. The adjoined group corresponding to the above structure is, however, continuous, and consequently not every group of this structure is necessarily discontinuous. Nevertheless, the group $p_1, p_2, x_1 p_2 - x_2 p_1 + p_3$, of the above structure, is discontinuous.* Its finite equations in the canonical form are

$$\begin{aligned} x'_1 = {} & \frac{x_1}{2}\left(e^{a_3\sqrt{-1}} + e^{-a_3\sqrt{-1}}\right) - \frac{a_1\sqrt{-1}}{2\,a_3}\left(e^{a_3\sqrt{-1}} - e^{-a_3\sqrt{-1}}\right) \\ & + \frac{x_2\sqrt{-1}}{2}\left(e^{a_3\sqrt{-1}} - e^{-a_3\sqrt{-1}}\right) + \frac{a_2}{2\,a_3}\left(e^{a_3\sqrt{-1}} + e^{-a_3\sqrt{-1}} - 2\right), \\ x'_2 = {} & \frac{x_2}{2}\left(e^{a_3\sqrt{-1}} + e^{-a_3\sqrt{-1}}\right) - \frac{a_2\sqrt{-1}}{2\,a_3}\left(e^{a_3\sqrt{-1}} - e^{-a_3\sqrt{-1}}\right) \\ & - \frac{x_1\sqrt{-1}}{2}\left(e^{a_3\sqrt{-1}} - e^{-a_3\sqrt{-1}}\right) - \frac{a_1}{2\,a_3}\left(e^{a_3\sqrt{-1}} + e^{-a_3\sqrt{-1}} - 2\right), \\ x'_3 = {} & x_3 + a_3. \end{aligned}$$

* This is one of the real groups of Euclidean movement in three dimensional space. Cf. Transformationsgruppen, III. 385.

If this transformation is denoted by T_a, then from the symbolic equation $T_b\,T_a = T_c$ we obtain the five relations

$$
\begin{aligned}
(27)\quad e^{c_3\sqrt{-1}} + e^{-c_3\sqrt{-1}} &= \tfrac{1}{2}\left(e^{b_3\sqrt{-1}} + e^{-b_3\sqrt{-1}}\right)\left(e^{a_3\sqrt{-1}} + e^{-a_3\sqrt{-1}}\right)\\
&\quad + \tfrac{1}{2}\left(e^{b_3\sqrt{-1}} - e^{-b_3\sqrt{-1}}\right)\left(e^{a_3\sqrt{-1}} - e^{-a_3\sqrt{-1}}\right),
\end{aligned}
$$

$$
\begin{aligned}
(28)\quad e^{c_3\sqrt{-1}} - e^{-c_3\sqrt{-1}} &= \tfrac{1}{2}\left(e^{b_3\sqrt{-1}} + e^{-b_3\sqrt{-1}}\right)\left(e^{a_3\sqrt{-1}} - e^{-a_3\sqrt{-1}}\right)\\
&\quad + \tfrac{1}{2}\left(e^{b_3\sqrt{-1}} - e^{-b_3\sqrt{-1}}\right)\left(e^{a_3\sqrt{-1}} + e^{-a_3\sqrt{-1}}\right),
\end{aligned}
$$

$$
(29)\quad c_3 = a_3 + b_3,
$$

$$
\begin{aligned}
(30)\quad & \frac{c_2}{2\,c_3}\left(e^{c_3\sqrt{-1}} + e^{-c_3\sqrt{-1}} - 2\right) - \frac{c_1\sqrt{-1}}{2\,c_3}\left(e^{c_3\sqrt{-1}} - e^{-c_3\sqrt{-1}}\right)\\
&= \frac{b_2}{2\,b_3}\left(e^{b_3\sqrt{-1}} + e^{-b_3\sqrt{-1}} - 2\right) - \frac{b_1\sqrt{-1}}{2\,b_3}\left(e^{b_3\sqrt{-1}} - e^{-b_3\sqrt{-1}}\right)\\
&+ \tfrac{1}{2}\left(e^{b_3\sqrt{-1}} + e^{-b_3\sqrt{-1}}\right)\\
&\times \left\{\frac{a_2}{2\,a_3}\left(e^{a_3\sqrt{-1}} + e^{-a_3\sqrt{-1}} - 2\right) - \frac{a_1\sqrt{-1}}{2\,a_3}\left(e^{a_3\sqrt{-1}} - e^{-a_3\sqrt{-1}}\right)\right\}\\
&+ \frac{\sqrt{-1}}{2}\left(e^{b_3\sqrt{-1}} - e^{-b_3\sqrt{-1}}\right)\\
\times & \left\{-\frac{a_2\sqrt{-1}}{2\,a_3}\left(e^{a_3\sqrt{-1}} - e^{-a_3\sqrt{-1}}\right) - \frac{a_1}{2\,a_3}\left(e^{a_3\sqrt{-1}} + e^{-a_3\sqrt{-1}} - 2\right)\right\} \equiv \chi,
\end{aligned}
$$

$$
\begin{aligned}
(31)\quad & \frac{c_1}{2\,c_3}\left(e^{c_3\sqrt{-1}} + e^{-c_3\sqrt{-1}} - 2\right) + \frac{c_2\sqrt{-1}}{2\,c_3}\left(e^{c_3\sqrt{-1}} - e^{-c_3\sqrt{-1}}\right)\\
&= \frac{b_1}{2\,b_3}\left(e^{b_3\sqrt{-1}} + e^{-b_3\sqrt{-1}} - 2\right) + \frac{b_2\sqrt{-1}}{2\,b_3}\left(e^{b_3\sqrt{-1}} - e^{-b_3\sqrt{-1}}\right)\\
&+ \tfrac{1}{2}\left(e^{b_3\sqrt{-1}} + e^{-b_3\sqrt{-1}}\right)\\
&\times \left\{\frac{a_1}{2\,a_3}\left(e^{a_3\sqrt{-1}} + e^{-a_3\sqrt{-1}} - 2\right) + \frac{a_2\sqrt{-1}}{2\,a_3}\left(e^{a_3\sqrt{-1}} - e^{-a_3\sqrt{-1}}\right)\right\}\\
&+ \frac{\sqrt{-1}}{2}\left(e^{b_3\sqrt{-1}} - e^{-b_3\sqrt{-1}}\right)\\
&\times \left\{\frac{a_2}{2\,a_3}\left(e^{a_3\sqrt{-1}} + e^{-a_3\sqrt{-1}} - 2\right) - \frac{a_1\sqrt{-1}}{2\,a_3}\left(e^{a_3\sqrt{-1}} - e^{-a_3\sqrt{-1}}\right)\right\} \equiv \psi.
\end{aligned}
$$

Denoting the right-hand members of equations (30) and (31) by χ and ψ respectively, and solving for c_1, c_2, c_3, we have

$$c_1 = \frac{a_3 + b_3}{2} \left\{ \frac{\sqrt{-1}\,(e^{\frac{1}{2}(a_3+b_3)\sqrt{-1}} + e^{-\frac{1}{2}(a_3+b_3)\sqrt{-1}})}{(e^{\frac{1}{2}(a_3+b_3)\sqrt{-1}} - e^{-\frac{1}{2}(a_3+b_3)\sqrt{-1}})}\,\chi - \psi \right\},$$

$$(32) \quad c_2 = -\frac{a_3 + b_3}{2} \left\{ \chi - \sqrt{-1}\,\psi \frac{(e^{\frac{1}{2}(a_3+b_3)\sqrt{-1}} + e^{-\frac{1}{2}(a_3+b_3)\sqrt{-1}})}{(e^{\frac{1}{2}(a_3+b_3)\sqrt{-1}} - e^{-\frac{1}{2}(a_3+b_3)\sqrt{-1}})} \right\},$$

$$c_3 = a_3 + b_3.$$

If the a's and b's are so chosen that χ and ψ are different from zero, and $a_3 + b_3 = 4\,k\,\pi$, where k is an arbitrary integer, both c_1 and c_2 become infinite. Consequently this group is discontinuous.

On pages 106–107, 384, Vol. III., Transformationsgruppen, Lie enumerates all possible types of real projective groups of the plane. I have examined all the two-, three-, and four-parameter groups in this list, and find that the groups

$$x_1 p_2, \quad x_1 p_1 - x_2 p_2, \quad x_2 p_1,$$

and

$$p_1 + x_1^2 p_1 + x_1 x_2 p_2, \quad p_2 + x_1 x_2 p_1 + x_2^2 p_2, \quad x_2 p_1 - x_1 p_2,$$

and these only, are discontinuous.

The first of these groups is the special linear homogeneous real group, and has the structure

$$(X_1, X_2) \equiv -2\,X_1, \ (X_1, X_3) \equiv X_2, \ (X_2, X_3) \equiv -2\,X_3.$$

The determinant Δ corresponding to this structure is

$$\Delta = \frac{e^{2\sqrt{a_2^2 + a_1 a_3}} - 1}{2\sqrt{a_2^2 + a_1 a_3}} \cdot \frac{e^{-2\sqrt{a_2^2 + a_1 a_3}} - 1}{-2\sqrt{a_2^2 + a_1 a_3}}.$$

This vanishes if the a's are so chosen as to satisfy the condition

$$a_2^2 + a_1 a_3 = -k^2 \pi^2,$$

where k is an arbitrary integer.*

The second of the above groups has the structure

$$(X_1, X_2) \equiv X_3, \quad (X_1, X_3) \equiv -X_2, \quad (X_2, X_3) \equiv X_1.$$

The Δ corresponding to this structure is

* The special linear homogeneous *complex* group has been shown to be discontinuous by Professor Study, Leipziger Berichte, 1892; and the *real* group by Professor Taber, Bull. Am. Math. Soc., April, 1896. The *general* linear homogeneous (real or complex) group is continuous. Thus a group may be continuous and yet have a discontinuous sub-group.

$$\Delta = \frac{e^{\sqrt{-(a^2_1+a^2_2+a^2_3)}}-1}{\sqrt{-(a^2_1+a^2_2+a^2_3)}} \cdot \frac{e^{-\sqrt{-(a^2_1+a^2_2+a^2_3)}}-1}{-\sqrt{-(a^2_1+a^2_2+a^2_3)}},$$

and this vanishes if the a's satisfy the condition $a^2_1 + a^2_2 + a^2_3 = 4\,k^2\,\pi^2$, where k is an arbitrary integer. The adjoined of this group is

$$a_1\frac{\partial}{\partial a_3} - a_3\frac{\partial}{\partial a_1}, \quad a_3\frac{\partial}{\partial a_2} - a_2\frac{\partial}{\partial a_3}, \quad a_2\frac{\partial}{\partial a_1} - a_1\frac{\partial}{\partial a_2},$$

and is discontinuous. Consequently, every group of this type is discontinuous.

In the table on pages 391–397, Vol. XXXV., of These Proceedings, as mentioned above, I have marked by an asterisk those types of structure for which all real groups are continuous; and by a dagger those types of structure for which I have found at least one real group that is discontinuous.

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VOL. XXXVI. NO. 7. — AUGUST, 1900.

CONTRIBUTIONS FROM THE HARVARD MINERALOGICAL MUSEUM.

VIII. — *ON HARDYSTONITE AND A ZINC SCHEFFERITE FROM FRANKLIN FURNACE, N. J.*

BY JOHN E. WOLFF.

WITH A NOTE ON THE OPTICAL CONSTANTS OF THE SCHEFFERITE.

BY DR. G. MELCZER.

CONTRIBUTIONS FROM THE HARVARD MINERALOGICAL MUSEUM.

VIII.—ON HARDYSTONITE AND A ZINC SCHEFFERITE FROM FRANKLIN FURNACE, NEW JERSEY.

By John E. Wolff.

WITH A NOTE ON THE OPTICAL CONSTANTS OF THE SCHEFFERITE.

By Dr. G Melczer.

Received June 21, 1900.

a. Hardystonite.

The new mineral *hardystonite* described in these Proceedings * was found in small grains in a mass of zinc ore and isolated by handpicking and the use of heavy solutions, while the (tetragonal) crystal system was determined by the study of thin sections of the grains. When visiting the mine in September, 1899, I received from the mine officials pieces from a large mass of nearly pure Hardystonite, several inches in diameter, which had been found in the same workings as the original mineral. The material is grayish-white in color, often streaked or clouded by faint pinkish tints, and breaks into angular fragments owing to the presence of several cleavages; the lustre is glassy on the more perfect cleavages, elsewhere faintly resinous. It was easy to select material for thin sections oriented parallel to the basal and prismatic cleavages and for polished plates parallel to the base, from which the indices of refraction were determined and the original statement confirmed; namely, that the mineral is tetragonal and optically negative, has a basal cleavage and primatic cleavages parallel to the prisms of the first and second orders — in addition, traces of a pyramidal cleavage were observed.

By means of the Abbé total reflectometer the indices of refraction were determined on a plate parallel to the base as follows:

* These Proceedings, XXXIV. 479, 1899.

For Na $\omega = 1.6691$ For Li $\omega = 1.6758 \pm .0002$

$\epsilon = 1.6568$ $\epsilon = 1.6647 \pm .0002$

The figures for Li are inaccurate in the fourth decimal to two or more places, owing to the indistinctness of the boundary line.

Unlike the original material, the mineral gives a strong sodium flame, and the following analysis of the new material (I) was therefore made: *

	I.	II.	III.	IV.	V.
SiO_2	37.78	37.73	624	624	38.10
Al_2O_3	0.91	0.91	8	313	0.57
Fe_2O_3	0.43	0.43	2		
ZnO	23.38	23.35	286		24.30
MnO	1.26	1.25	17		1.50
CaO	34.22	34.19	610	616	33.85
MgO	0.26	0.26	6		1.62
K_2O	0.78	0.78	8	25	....
Na_2O	1.10	1.10	17		....
Ig	0.34	....	...	...	0.52
	100.46	100.00	...	...	100.46

I. Analysis of new material.
II. Analysis of new material reduced to 100 omitting *Ig*.
III. and IV. Molecular proportions.
V. Analysis of original material.

It is seen that the alkalies replace in part the Ca and Mg, but that there is still a molecular excess of the alkalies. The thin sections show, in addition to numerous fluid inclusions, the presence of frequent small grains of an undetermined mineral to which the content in alkalies may be partly due.

* Both analysis and optical determinations were made by me in the Mineralogical Institute at Munich.

b. Zinc Schefferite.

While visiting the mine in September, 1898, my attention was called by Mr. Van Mater, Superintendent at North Mine Hill, to a peculiar pyroxene which was then coming out from the workings at the Parker Shaft, and abundant material was then secured from the ore sorting belts in the concentrating mill. The mineral occurs in large foliated masses, associated with franklinite, willemite, and small grains and masses of a white zinc mineral (to be described in the future), which often lies in thin films parallel to the basal planes of the pyroxene. The latter has a light-brownish red color in the large masses, while another variety occurring in small grains in the zinc ore has a deep brown color. The most striking physical feature is the (apparent) basal cleavage, which is as perfect as that of feldspar, in addition to the ordinary prismatic pyroxene cleavage.

The angle between the two prismatic cleavages was determined by the reflecting goniometer as 92° 59′, between the basal cleavage and the prism as 79° 02′. In a thin section parallel to (010) the angle β between the basal cleavage and c′ was determined as 74° 25′. It is readily seen in this clinopinacoidal section that the apparent cleavage parallel to the base is due to the development of gliding planes, for the basal cleavage planes enclose thin lamellae which are evidently in the position of twins parallel to the base with reference to the main mass of the mineral.

The thin sections show the usual optical character of monoclinic pyroxene, — one optic axis is approximately perpendicular to the base; on the clinapinacoid the axis of least elasticity $\mathfrak{c}$ makes an angle of 40° 35° with c′, lying in the obtuse angle β.

The following analysis shows that the mineral is a zinc schefferite; it was found impossible to completely decompose the mineral with HF, hence FeO was not determined.

SiO_2	52.86
$Fe_2O_3 + Al_2O_3$	1.08
MnO	5.31
ZnO	3.38
MgO	13.24
CaO	24.48
Ig	0.45
	100.80
Sp. Gr.	3.31

Optical Constants of the Schefferite.

By Dr. Gustave Melczer.

The indices of refraction were determined on polished plates, prepared by Voigt & Hochgesang, by means of the Abbé total reflectometer and with the application of the differential method proposed by Viola.* There were used (1) a plate approximately perpendicular to the acute bisectrix, (2) a thin section similarly oriented, and (3) and (4) two plates parallel to the base (001). Since the plates were not transparent, the boundaries of the total reflection could only be measured with the reducing telescope, but with this, especially in the case of the last two plates (owing to their excellent polish), the limits could be fixed within 1 to 3 minutes. By reading every 15 degrees and in the vicinity of the maxima and minima every 5 degrees (which according to my experience completely suffices with the reducing telescope), the boundary curve was constructed, and the following maxima and minima determined for Na light:

(1)	↑ 64° 26½′ and	64° 22′	62° 56′ and	62° 26′
(2)	?	?	62° 57¾′	62° 27½′
(3)	64° 25′	64° 1¼′	62° 55′	62° 23½′
(4)	64° 20¾′	64° ½′	62° 51¾′	62° 23′

The boundaries for the comparison prism were determined, after each pyroxene determination, by five readings 90° apart, as follows:

(1) 62° 11′ (2) 62° 10½′ (3) 62° 11¾′. (4) 62° 11½′

The cause of these noticeable differences in ω of the prism cannot lie in the temperature, for this only differed by 3° on the different days when the measurements were made, nor can it be due to lack of homogeneity in the glass hemisphere, for in using the enlarging telescope the mean of two readings in diametrically opposite positions of the horizontal circle were only 15 seconds apart. The cause can therefore only lie in the use of the reducing telescope itself, the accuracy of which, even with the sharpest boundaries, is only within 1 to 1½ minutes, while with the enlarging telescope the same boundaries can be determined within 10 to 15 seconds.

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* Zeit. für Kryst., XXX. 438 and XXXII. 313.

As regards the differences between the boundary angles of the individual plates, these are too large to be ascribed to indefiniteness of the boundary lines, for as already mentioned these were sharp, especially in (3) and (4). In order to be quite sure I repeated the measurements on three plates and found:

					Prism.
(1)	↑ 64° 27¾′ and 64° 23¼′	→	62° 57½′ and	62° 29′	62° 10½′
(2)	64° 21′	. . .	62° 54½′	62° 24½′	62° 12′
(3)	64° 21′	. . .	62° 51¾′	62° 21¼′	62° 11′

There the above supposition was correct.

Since the refractive index of the glass of the Abbé hemisphere, according to one of my previous determinations, is 1.8903 for Na light, and that of the glass prism used 1.6724, there follows from the boundary angles given above for the individual plates:

	γ_{na}	β_{na}	α_{na}
(1) and (2)	1.7060 ± 0.0002	1.6840 ± 0.0002	1.6766 ± 0.0004
(3)	1.7050 ± 0.0005	1.6834 ± 0.0001	1.6757 ± 0.0001
(4)	1.7045 ± 0.0001	1.6827 ± 0.0001	1.6752 ± 0.0002

and as a mean: $\gamma - \beta = 0.0218$
$\beta - \alpha = 0.0075$
$\gamma - \alpha = 0.0293$

These variations of the indices in the individual plates could perhaps be referred to local variations in the chemical composition of the zinc schefferite, or to the uneven distribution of pigment. The latter is not noticeably different, and yet it is known that for certain minerals at least very small variations produce such differences in the indices.

If from the above values we take as the mean of the indices

$$\gamma = 1.705$$
$$\beta = 1.683$$
$$\alpha = 1.676$$

then by calculation 2 V_a for sodium = 59° 29¼′.

For the direct measurement of the axial angle the plate (1) could not be used, for although one optic axis and the middle of the figure could be seen, and therefore, H_1 might have been measured, yet the geometric orientation of the surface could not be determined; the thin section (2) gave both hyperbolas, but somewhat indistinctly, so that they could only

be centred within $\frac{1}{2}°$ accuracy. The plate was immersed in monobromonapthalin whose temperature during the measurement was 19° and whose index of refraction was determined by the Abbé total-refractometer as: $n_{na} = 1.6597$. With the thin section the following values were determined in the axial angle apparatus:

	Li	Na	Tl
H_1	37° 30′	37° 20′	36° 50′
H_2	24° 10′	23° 40′	23° 40′

whence, as w_β for the section was found to be 62° 57′ 45″ and $\beta = 1.6842$:

$$2\ V_a \text{ for sodium} = 60°\ 0' \text{ and } \rho > v.$$

MUNICH, April, 1900.

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ON THE THERMAL AND ELECTRICAL CONDUCTIVITY OF SOFT IRON.

BY EDWIN H. HALL.

INVESTIGATIONS ON LIGHT AND HEAT MADE AND PUBLISHED WHOLLY OR IN PART WITH APPROPRIATIONS FROM THE RUMFORD FUND.

ON THE THERMAL AND ELECTRICAL CONDUCTIVITY OF SOFT IRON.

By Edwin H. Hall.

Received May 9, 1900. Presented July 17, 1900.

The general method used in the investigation of which this paper is to give an account is set forth with much detail in two articles already published.* Certain more or less important changes of apparatus or procedure will be described and discussed later; but the main results will first be given.

The metal studied was Taylor (Yorkshire) wrought iron, recommended to me by an engineer friend of much experience as the softest wrought iron to be found in the Boston market. Chemical analysis showed the following composition: —

Iron	99.93 %
Carbon	0.059

The density was about 7.785 at 0° C.

The values which I find for the thermal conductivity, k, of this iron are

at 0.1528	28°.2 C.
" 0.1514	58°.3 C.

if the specific heat of water at each of these temperatures is called 1. This would give for the temperature coefficient 0.0003, very nearly.

If the values of k are revised in accordance with the values proposed by Winkelmann † for the specific heat of water at the given temperatures, they become

at 0.1513	28°.2 C.
" 0.1511	58°.3 C.

---

* Thermal Conductivity of Mild Steel, by E. H. Hall, These Proceedings, XXXI. 271, 1896; On the Thermal Conductivity of Cast Iron, by E. H. Hall and C. H. Ayres, XXXIV. 283, 1899.

† Part 2 of Vol. II. p. 340.

and the temperature coefficient deduced therefrom will be too small to be worth writing down, 0.0000?, let us say.

But the recent work of Callendar and Barnes* gives for the specific heat of water

0.9992	at 25° C.
0.9987	" 30° C.
0.9992	" 55° C.
1.0000	" 60° C.

If these values given by Callendar and Barnes are adopted as correct, my first values of k will stand almost without change; and I shall therefore leave them for the present without correction for variation in the specific heat of water.

My value for the temperature coefficient, 0.0003 or a little less, is, so far as it goes, a corroboration of the substantial accuracy of the temperature coefficient found by Lorenz, 0.0002282, although it may be doubted whether the last three figures of this number are of much significance. This agreement is eminently satisfactory to myself; for a comparison of the work of Lorenz with that of other investigators has convinced me that his value of the temperature coefficient is entitled to an especial degree of confidence.

Measurements of the electrical resistance of the iron were made on nine cylinders, each 2 cm. long and about 0.23 cm. in diameter, cut from the same great bar as the disk on which the measurements of k were made. The length of the cylinders, like the thickness of the disk, was taken parallel to the length of the bar; and the cylinders were cut from a part of the bar adjacent to that from which the disk was cut. The extreme difference in the specific resistances of these cylinders was apparently about 5 per cent. The mean specific resistance was found to be 12240 at 18° C. The mean specific conductivity, x, at the same temperature would, therefore, be 817×10^{-7} C. G. S.

The ratio $k \div x$ is about 1716 at 0° C.

The "thermo-electric height" of this iron, as compared with copper, is about

1028×10^{-8} volts at	26°.6 C.
980 " " "	41°.3 C.
936 " " "	54°.5 C.
870 " " "	71°.1 C.

* Physical Review, April, 1900.

The relation of the values here given for k and x to those found by others who have studied the thermal and electrical conductivities of soft iron, I have set forth in the "Physical Review" for May–June, 1900.

The following details of my work are perhaps unnecessarily extended and tedious; but a considerable study of the literature of thermal conductivity has convinced me that most experimenters in this field have omitted important matters in the printed description of their investigations. It is my hope that those who may have to deal with problems similar to, though not exactly like mine, will find what is here written worthy of their attention.

The iron used for the experiments on thermal conductivity was in the form of a disk cut from the end of a five-inch cylinder and turned down at first to a diameter of 10.5 cm. The thickness of the disk was about 1.996 cm., the greatest thickness indicated by the calipers being 1.998 cm., and the least 1.995 cm.

Treatment of the Disk.

The disk was coated with copper electrolytically on both faces by a method substantially the same as that previously described. Spots which, because of slight flaws in the surface, appeared not to be taking the copper well from the preliminary cyanide bath, were rubbed with the point of a lead pencil to give them a coating of graphite, after which they speedily became coppered like the rest. In the sulphate bath the convex surface of the disk was protected as before by rubber bands; but outside these bands was now placed a band of paraffined paper about 5 cm. wide, the object of which was to impede the deposit at the edge of the faces of the disk and so make it keep better pace with the rate of deposit at the centre of the faces. As before, it was occasionally necessary during the progress of the deposit, which lasted about a week, to remove the disk from the bath in order to break off or file off projecting pimples, or *corals*, of copper.

The final coating of copper on each face, after being turned down nearly to a plane, was about 0.2 cm. thick. The whole curved surface was now turned down until the diameter of the disk was 10.00 cm.

Mounting and Use of Disk and Adjacent Apparatus.

Figures 1 and 2 of an article already mentioned, "On The Thermal Conductivity of Cast Iron," indicate with accuracy in most particulars

the method of mounting and using the disk now under consideration. Certain small changes, however, must be imagined in Figure 2, in order to make it accord perfectly with the latest developments of the apparatus. Thus, the water stream entering beneath the disk is no longer allowed to flow without restriction straight against the centre of the lower face. A little affair shaped somewhat like a three-legged stool is placed at the top of the admission tube, just beneath the point marked by the letter C′, and most of the water escapes laterally between the legs of the stool, although a small part of it runs through a hole in the top straight against the disk. This device was adopted in the hope that it would make the temperature more uniform over the lower face of the disk. With a similar purpose regarding the upper face of the disk, the hard rubber block HH has been replaced by one having a somewhat more gradual curvature, so as to make a thinner and more rapid stream over the central parts of the disk. It is doubtful whether these changes have done much good, on the whole, although they appear to have made the difference of temperature between top and bottom of disk at the centre very nearly equal to the mean difference at other parts, as numbers presently to be given will show. Another attempt to improve the distribution of temperature, by making the flow of water more nearly equal along different radii of the upper face of the disk, affected the manner of admission of the water to the funnel FF; but, as it was of doubtful utility, it need not be described. The air-vent leading up from the funnel FF by the tube w has been considerably enlarged; but the small escape of water which had previously been maintained at this vent is no longer permitted.

The small copper wires, extending from the copper coatings of the disk, are now protected from actual contact with the hard rubber plugs K_1, K_2, etc., and with the soft rubber packing surrounding these plugs, by a wrapping of oiled silk, with the purpose of preserving the wires from the destructive action of the sulphur emitted from the rubber; but, after all, the wires cannot be depended upon for more than a few months.

Stops about 0.16 cm. thick, placed at the edges of the faces of the disk, prevent the blocks HH and H′H′ from approaching these faces so near as to endanger the safety of the small wires or cut off the flow of water.

The parts marked J_1 and J_2 in Figure 2 of the former paper now contain spirals of platinum instead of thermo-electric junctions of copper and German silver, change of resistance of platinum having been substituted for change of thermo-electromotive force as a means of measuring

the change of temperature of the stream of water which flows over the upper surface of the disk. More will be said of this later. The parts surrounded by the water-jacket are carefully and thickly wadded with cotton-wool so as to make a nearly cylindrical body, about 18 cm. in diameter, up to the plugs J_1 and J_2. The plugs also are covered with cotton-wool, as well as the slot in the top of the jacket. Around the disk itself the wadding is so thick as barely to allow the jacket to enclose it.

The copper wires leading out from the plugs J_1 and J_2 ran, after July 17, outside the cotton-wool wrapping, but without touching the jacket.

Determination of the Difference of Temperature of the Two Faces of the Disk.

As before, this is effected by thermo-electric means, the iron disk and its two copper coatings being used as a thermo-electric couple. As before, thirteen fine copper wires lead off from as many points on the upper coating, and similar wires from corresponding points on the under coating. Each pair of corresponding wires can be used singly, or all the thirteen pairs can be joined and used in multiple by an arrangement described in a preceding paper. The distribution of wires over either coating is shown in Figure 1, the numerals being alongside the points of attachment to the coating.

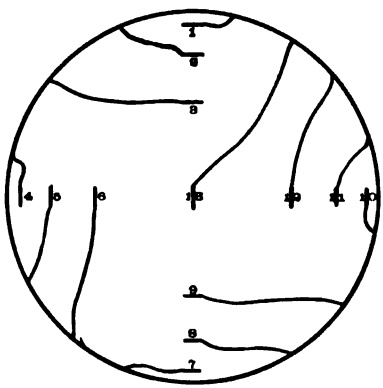

Figure 1.

In the arrangement of these points there was an attempt to make the various areas represented respectively by the individual points as nearly equal as practicable. Point 13 is intended to be at the centre of the disk; points 3, 6, 9, and 12, 2.55 cm. from the centre of the disk; points 2, 5, 8, and 11, 3.80 cm. from the centre of the disk; points 1, 4, 7, and 10, 4.60 cm. from the centre of the disk.

No great accuracy is attained in placing these points; and, in fact, each attachment is rather a line, about 0.5 cm. long, than a point, each such line, except No. 13, crossing nearly at right angles the radius upon which it lies.

It is, of course, desirable to make the flow of water along the two faces of the disk such that the indication received from any one pair of wires, one above and one below, shall be about the same as that given by any other such pair of wires, and much thought has been given to the attainment of this end. The result is not quite all that could be wished for; but it is such that any important error from the inequalities observed is very unlikely. The following tables show the results of tests made under conditions as nearly uniform as it was found practicable to keep them. The galvanometer deflection credited to each pair of junctions is the mean obtained from two short sets of observations, the various pairs being used first in the order in which they are here given, and then in the reverse order. Between these forward and back series of observations with single pairs a short set of observations with all the pairs in multiple was made, and the mean deflection from this set, corrected for the difference of resistance of the multiple and single arrangements, is also given below.

Temperature about 28° *C.*

Junctions.	Deflections.	
13 and 13′	11.1	
1 and 1′	11.0	11.6
4 and 4′	11.1	
7 and 7′	12.0	
10 and 10′	12.2	
2 and 2′	10.9	11.3
5 and 5′	10.8	
8 and 8′	11.7	
11 and 11′	11.6	
3 and 3′	10.6	10.7
6 and 6′	10.7	
9 and 9′	10.5	
12 and 12′	11.1	
Mean,	11.2	

Along radii		
1 and 1′	11.0	10.8
2 and 2′	10.9	
3 and 3′	10.6	
4 and 4′	11.1	10.9
5 and 5′	10.8	
6 and 6′	10.7	
7 and 7′	12.0	11.4
8 and 8′	11.7	
9 and 9′	10.5	
10 and 10′	12.2	11.6
11 and 11′	11.6	
12 and 12′	11.1	

All in multiple, 11.3

Temperature about 57° C.

Junctions.	Deflections		Along radii.		
13 and 13′	10.4				
1 and 1′	11.5	10.7	1 and 1′	11.5	11.3
4 and 4′	9.5		2 and 2′	11.5	
7 and 7′	10.8		3 and 3′	11.0	
10 and 10′	10.8				
			4 and 4′	9.5	9.6
2 and 2′	11.5	10.7	5 and 5′	9.5	
5 and 5′	9.5		6 and 6′	9.7	
8 and 8′	10.6				
11 and 11′	11.3		7 and 7′	10.8	10.4
			8 and 8′	10.6	
3 and 3′	11.0	10.3	9 and 9′	9.9	
6 and 6′	9.7				
9 and 9′	9.9		10 and 10′	10.8	19.0
12 and 12′	10.6		11 and 11′	11.3	
Mean,	10.5		12 and 12′	10.6	

All in multiple, 10.4

It seems likely that the differences between the different radii are due in part to inequalities of water-flow caused by the lodging of air-bubbles at various points on or near the surfaces of the disk.

The agreement between the deflection obtained with all junctions in multiple and the mean of those obtained with the pairs used singly appears satisfactory, in view of the not very rigid character of the test by which the comparison is made.

The resistance of each individual pair of wires, out to the point where all were connected in multiple, is shown in the following table, as it was found July 12th, 1899: —

13–13′	0.56 ohm	8– 8′	0.56 ohm
1– 1′	0.55 "	11–11′	0.56 "
4– 4′	0.55 "	3– 3′	0.55 "
7– 7′	0.56 "	6– 6′	0.56 "
10–10′	0.56 "	9– 9′	0.55 "
2– 2′	0.55 "	12–12′	0.56 "
5– 5′	0.56 "		

The deflections noted above are those of a rather sensitive astatic galvanometer, the sensitiveness of which was frequently determined by means of a potentiometer and a standard Carhart cell, or rather, two

such cells, which differed from each other in electromotive force about 1 part in 500.

The mean difference of temperature of the two streams of water on entering the apparatus was about 8° at low temperatures and about 7°.6 at high temperatures. The mean difference of temperature between the two surfaces of contact of the iron and copper, as indicated thermo-electrically, was about 1°.42 at low temperatures and about 1°.58 at high temperatures, which shows that heat is communicated more readily from the water to the copper coatings, and *vice versa,* at high temperatures than at low temperatures, other things being equal.

In order to determine the difference of temperature, just mentioned, between the surfaces of contact of the copper with the iron disk, it was of course necessary to find the thermo-electromotive force corresponding to a known difference of temperature of two similar junctions. This datum was obtained by the method described in Appendix I of the paper on the "Conductivity of Cast Iron," to which paper a number of references have already been made in this writing. Some particulars of the present case follow.

A second disk about 2.5 cm. thick was cut from the same end of the same cylinder of Yorkshire iron that had furnished the disk already described. This second disk was then cut into two half disks, and from one of them was taken a slice, thickness-wise, about 11 cm. long, 2.5 cm. wide, and 0.3 cm. thick. This slice was then sawed up, crosswise, into thirty-three bars. All but ten of these bars were then reduced by filing and milling to a diameter of about 0.16 cm., and the length of each was reduced to 2.0 cm. The remaining ten were reduced in the same way to a thickness of 0.23 cm. and a length of 2 cm. The bars were then numbered from 1 to 33 in the order of their original position in the slice from which they had been cut. Numbers 1, 4, 7, 10, 13, 20, 23, 26, 29, and 32 were placed end to end, in the order just given, in the bore of the wooden cylinder of the thermo-electric test apparatus shown in Figure 5 of the article on "Conductivity of Cast Iron." No essential change has been made in this apparatus or in the manner of using it since the description given in the article just mentioned was written, except in these particulars, that the electrical resistance * of the end-to-end row of bars

* This resistance was likely to be as much as 2.5 or 3 ohms when the pressure, about 3 kgms., was newly applied to the row, but a gentle rocking, from side to side, of the copper blocks, kept well seated, would in the course of a few minutes reduce this resistance to less than 1 ohm, the end pressure remaining un-

and copper end-pieces has been dealt with more carefully and successfully in recent experiments than in earlier ones, and that in some cases the bars have been placed in a glass tube instead of a wooden one. The results of these thermo-electric tests, subject to slight corrections for peculiarities of the thermometers * used, are given below. The temperature put down for each case, in the second column, is the mean of the thermometer readings in the two copper blocks at the ends of the row of iron bars. The third column, headed Δ, gives for each case the mean difference of temperature of the two thermometers. The fourth column, headed E, gives for each case the thermo-electromotive force corresponding to a difference of 1° between the two thermometers, each of which thermometers is supposed to indicate with sufficient accuracy the temperature of the copper-iron contact neighboring to it.

Date	T		Δ		E	
June 3, '99	25°.8		7°.04		1041 × 10⁻⁸	
" 7, "	27°.7		7°.52		1017 "	
" 30, "	25°.3	26°.6	7°.61	7°.30	1024 "	1028×10^{-8} volt
July 3, "	26°.5		8°.22		1042 "	
" 4, "	26°.4		6°.64		1031 "	
" 6, "	27°.8		6°.79		1012 "	
June 6, "	40°.5		7°.44		979 "	
" 7, "	44°.6		7°.23		964 "	
July 3, "	40°.6	41°.3	7°.79	7°.19	982 "	978×10^{-8}
" 4, "	38°.8		6°.94		990 "	
" 6, "	42°.0		6°.57		976 "	
June 6, "	55°.6		7°.03		926 "	
" 7, "	56°.5		6°.95		930 "	
July 3, "	52°.2	54°.5	7°.60	6°.89	941 "	934×10^{-8}
" 4, "	53°.8		6°.64		938 "	
" 6, "	54°.6		6°.25		933 "	
June 3, "	69°.0		6°.07		885 "	
" 7, "	74°.5		6°.24		850 "	
" 30, "	69°.4	71°.1	6°.18	6°.37	865 "	871×10^{-8}
July 3, "	70°.6		7°.04		874 "	
" 4, "	71°.3		6°.04		879 "	
" 6, "	71°.9		6°.66		870 "	

changed, and, except during the moments of measurement of resistance, no electric current flowing through the row of bars.

* Baudin, Nos. 10,286 and 10,287, as in previous work.

Applying to the mean values of E, found above, certain small corrections which take account of errors in the graduation of the thermometers, we get, —

T	E
26°.6	1028×10^{-8} volt
41°.3	980 " "
54°.5	936 " "
71°.1	870 " "

These numbers plotted, with temperatures for abscissas and electromotive force per degree for ordinates, indicate a curve which descends with very gradually increasing slope with rise of temperature. Indeed, this curve is so nearly a straight line that its curvature cannot be satisfactorily shown in a small figure. It would be almost perfectly straight if the numbers given under E were 1028, 975, 929, and 870.

The minute examination which I was obliged to give to the individual small cylinders, during measurements of their electrical resistance, led me to notice defects and possible distortions which might, I feared, have affected their thermo-electric quality. Accordingly, several months after tests just described were made, I undertook a similar test with ten of the somewhat larger cylinders already mentioned, which had apparently suffered much less in the process of milling. In this later test I found it convenient to enclose the bars in a tube of glass instead of a tube of wood. This test gave 1064×10^{-8} for E at 15°.4 C.

The earlier tests, above described, did not run so low in temperature, but by extrapolation they give, for 15°.4 C., $E = 1065 \times 10^{-8}$, or something very close to that, a satisfactory agreement.

Determination of the Difference of Temperature of the Ingoing and Outgoing Water at the Chamber above the Disk.

It has been already stated that a differential platinum thermometer was used for this purpose instead of the two copper-German-silver thermo-electric junctions which had been employed in the preceding investigations. This change was the result of a conviction, the fruit of much experience and vexation, that no suitable permanent protection can be found for the thermo-electric junctions against the action of hot water. A thin layer of shellac well dried on appears to be the best coating; but this is liable to give way at a most inconvenient time and bring to naught

the labor and observations of hours. The platinum thermometer method is not without difficulties, as the following pages will show; but it appears preferable to the other.

Figure 2 represents one of the platinum spirals, S, in position for use. It consists of about 22 cm. of wire, 0.012 cm. in diameter. The diameter of the coils is about 0.45 cm. The ends of this platinum wire are soldered

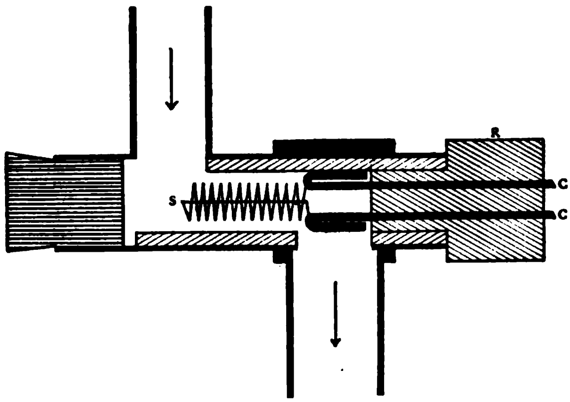

FIGURE 2.

to copper wires, C and C, each about 1.6 m. long and 0.1 cm. in diameter, which extend through the hard rubber plug R. Each of the copper wires is soldered at the outer end to a copper rod 5 cm. long and 0.6 cm. in diameter, which is well amalgamated at the free end and serves to make connection with a mercury well of a Carey Foster bridge. Care was taken to make the length of the wire very nearly equal in the two spirals, and equal care to make the copper wires, all of which are from the same piece, all alike at first. The parts of Figure 2 which are in solid black represent metal; the parts cross-hatched thus / represent soft rubber.

The resistance of each spiral was about 1.4 ohms, and that of its connecting copper wires about 0.1 ohm. Trial showed that one spiral with its connecting wires had a resistance about 0.0006 ohm greater than that of the other spiral and its connections. Slight changes in the copper wires reduced this difference of resistance to something like 0.000025 ohm. As the original difference of resistance was probably nearly all in the spirals, these continued to differ, at the temperature of the room, by something like 0.0006 ohm, which would correspond to about one-seventh part of a degree difference of temperature. No attempt at a

closer adjustment of the spirals was made, as the method of experimentation was expected to eliminate from the result any considerable error arising from this inequality. That this expectation was finally justified will be shown later, although more difficulty was encountered than at first appeared, the fact being, apparently, that the two spirals, although made from the same piece of wire, did not have quite the same temperature coefficient of resistance, so that the difference of resistance between them was not constant when their temperature was varied,* but increased when the spirals were heated.

Calibration of Differential Platinum Thermometer.

In order to calibrate this differential platinum thermometer, the two spirals were placed in streams of water, the temperatures of which were measured by means of the same thermometers that were used in studying the copper-iron thermo-electric junctions, and the difference between the electric resistance of spiral No. 1, with its connecting wires, and that of spiral No. 2, with its connecting wires, was measured by means of a Carey Foster bridge. The conditions under which this trial was made resembled very closely those under which the spirals were to be used in the main experiment, the plugs bearing the spirals being inserted in the same sockets in which they were afterward to be used, which sockets were temporarily removed from the main apparatus and fitted to brass tubes through which flowed the streams of water employed for the test; these tubes were wrapped around with cotton wadding, and sockets and tubes together were surrounded by the same water-jacket that was used later to surround the main apparatus. The copper connecting wires led down between the cotton wadding and the water-jacket, and then out beneath the latter without touching it; this detail is mentioned because the temperature of the connecting wires is by no means a matter of indifference in some parts of the investigation. In this calibration test each stream flowed past the thermometer bulb before reaching its spiral, and past the spiral before reaching the ends of the copper wires which carried the spiral. The distance from each thermometer bulb to the

* The wire from which the spirals was made was annealed by drawing it through a flame, which treatment may have introduced into it some lack of uniformity. After the spirals were formed and soldered to the copper they were kept in a bath of melted paraffine, in the neighborhood of 145° C., about two hours, with the object of removing inequalities of condition caused by the bending to which the wire had been subjected.

spiral beyond it was perhaps 2 cm. The velocity of the stream between the bulb and the spiral was some 30 or 40 cm. per second. One stream was usually about 6°.7 warmer than the other. The method of alternation was used; that is, if the stream passing spiral No. 1 was during one set of observations kept a certain number of degrees warmer than the other stream, the streams were exchanged at the end of that set and another set was then made, the difference of temperature and the mean temperature remaining nearly as before, and no part of the apparatus suffering change of place except the cock by means of which the change of flow was affected. The combination of the two complementary sets of observations gave a result from which errors due to disagreements of the thermometers and lack of perfect equality of the spirals was practically eliminated. Sets of observations were made at various mean temperatures, and, in order to make the results at these various temperatures comparable, slight corrections, amounting at the most to less than one-half of one per cent, were made in certain cases because of errors in the graduation of the thermometers, the combined diameters of the bores being slightly greater at some temperatures than at others. Similar corrections made in calibrating the copper-iron thermo-electric junctions have already been referred to.

Each of the horizontal lines, numbered from 1 to 8 in the table below, gives the result of two complementary sets of observations, such as have been described above. T is the mean temperature of each pair of sets; Δ is the mean difference of temperature of the streams; L is the mean length of bridge wire included between the two points of equilibrium corresponding to the two positions of the commutator of the Carey Foster bridge.

Date	T	Δ	L	L ÷ Δ	
May 5, 1899	20°.77	6°.68	20.30 cm.	3.039	(1)
" 6, "	36°.72	6°.33	19.21 "	3.032	(2)
" 11, "	70°.41	6°.55	19.86 "	3.032	(3)
" 11, "	21°.32	6°.99	21.20 "	3.033	(4)
" 12, "	76°.12	6°.63	20.21 "	3.048	(5)
" 17, "	51°.60	6°.80	20.57 "	3.024	(6)
" 26, "	52°.46	6°.96	21.01 "	3.018	(7)
" 26, "	37°.69	7°.15	21.59 "	3.019	(8)

The mean resistance of the bridge wire used in this test was 0.001491 ohm per cm., the material being German silver and the diameter about 0.2 cm. The mean resistance of the bridge wire, German silver about 0.4 cm. in diameter, employed in later experiments, when the spirals

were used to determine the change of temperature of water in the heat-conduction apparatus, was 0.0002548 ohm.* With these data we get from the table above:—

Mean of	T	$L \div \Delta$	l
(1) and (4)	21°.1	3.036	17.77
(2) " (8)	37°.2	3.026	17.71
(6) " (7)	52°.0	3.021	17.68
(3) " (5)	73°.3	3.040	17.79

Here l stands for $(L \div \Delta) \times (0.001491 \div 0.0002548)$, that is, the length of bridge wire, used in the main experiments, corresponding to a difference of 1° in the temperature of the spirals. Values of l for temperatures intermediate between those here given were found when needed by interpolation between the values of l here given. It will be observed that there is a maximum difference of 11 parts in 1770 between the given values of l. Rigid constancy of l would mean rigid constancy of the mean of the temperature coefficients of the two spirals with reference to the mean scale of the mercury thermometers used. Such constancy was hardly to be expected.

Use of Differential Thermometer in the Main Experiments.

In the main experiments the plugs bearing the spirals were at first placed in their supporting sockets according to Figure 2, which represents the spiral placed in the incoming stream. The water, therefore, on entering the apparatus, passed the first spiral before reaching its copper connections, but on leaving the apparatus it passed the copper connections of the second spiral before coming to the spiral itself. Accordingly, any net conveyance of heat by the copper wires into or out of the stream was superposed on the action of the conducting disk to produce the difference of temperature noted by the spirals. Any such effect of the copper wires would probably be very small except at high temperatures; and at such temperatures the effect would be, in large measure, eliminated from the result by the practice, always maintained, of combining one set of observations in which the disk carried heat to the upper stream with another set of observations in which the disk carried heat from the upper stream, the mean temperature of the disk re-

* Each bridge wire was calibrated by finding what length upon it corresponded to the difference between the resistance of a 1 ohm coil and that of a similar coil shunted by a known, much larger, resistance.

maining nearly unchanged throughout the two sets.* The elimination, however, would not be perfect; for the reason that the temperature of the stream which we are considering is not quite the same in the two complementary sets of observations just described, being about 8° warmer in one set than in the other. The question at issue comes, therefore, very nearly to this, whether the amount of heat carried away from the stream by the wires, when the stream is 8° warmer than the room, is negligible in comparison with the amount carried away by the disk, the difference of temperature of the two faces of the iron being, as we have seen, usually 1°.4 or more. This question can be answered in the affirmative; for the aggregate cross-section of the four copper wires is little, if any, more than 0.03 sq. cm., and the length of each wire, from the spiral out to the point where it is exposed to the temperature of the room, is not far from 30 cm. The carrying power for heat of a rod of copper 30 cm. long and 0.03 sq. cm. in cross-section, the thermal conductivity of copper being taken as eight times that of iron, would be about one five-thousandth part of the carrying power of the iron disk for a given difference of temperature, and not more than one eight-hundredth part, if the difference of temperature were 8° for the rod and 1°.4 for the disk. Nevertheless, after a considerable number of trials had been made with the spirals placed as in Figure 2, the plugs bearing the spirals were put in at the other ends of the supporting sockets, so that any changes of temperature produced in the stream by the copper wires must now occur either before or after the change of temperature noted by the spirals. The mean of the results obtained after this change of arrangement was slightly different from the mean of those obtained before; but it is unlikely that the difference was due to this change.

In the observations of July 31 and thereafter a loop of each copper wire was kept in a pocket containing oil on the outside of the water-jacket, so that each wire had at this point a temperature not more than one or two degrees different from that of the spiral with which it was connected.

Another question was whether the heat carried in or out by the copper wires affected the temperature of the spirals directly by metallic conduction, so as to keep them at a temperature different from that of the water passing them. The reasons for thinking that any such effect was negligible are given in the Appendix to this paper.

It has been stated that there was a difference of resistance between the two spirals at any given temperature, and that this difference in-

* The time between the exchange of the water streams and the beginning of the next set of observations was usually rather more than twenty minutes.

creased with rise of temperature. This difference, if constant at each temperature, would be eliminated by combining two sets of observations made at the same mean temperature, one set being made with spiral No. 1 the warmer, and the other with spiral No. 2 the warmer. Sets of observations were, it is true, combined in pairs, but in each such pair it was the mean temperature of the disk that was kept nearly constant, while the mean temperature of the spirals was seven or eight degrees warmer in one set than in the complementary set. Accordingly, the mean result of a pair of sets, taken without individual correction for the inequality of the spirals, would have been subject to the error caused by ignoring the variation of this inequality through a rise of, we will say, 8 degrees in mean temperature. This error would have been about 1.5 per cent of the final result at any temperature. To prevent such an error, corrections, based on careful observations made for this specific purpose, were applied in each individual set of observations for conductivity; and, after these corrections had been applied, the complementary sets were put together for a mean result at any given temperature of the disk. By this means the error in question was probably reduced to very small dimensions.

It appeared likely that some part of the apparent difference of resistance of the spirals at high temperatures was due to difference of resistance of the copper connecting wires, which near the spirals and for some distance away from the latter were considerably heated. As the experiments went on, increasing care was taken to make the condition of the wires leading to one spiral as nearly as might be the same as the condition of those leading to the other spiral, in order that the differential changes of resistance should be confined to the spirals themselves. The result was a progressive diminution of the correction for isothermal inequality of resistance at high temperatures; but this correction remained large and somewhat uncertain to the end, so that the value of the conductivity calculated from any one set of observations, unbalanced by its complementary set, was liable to a considerable error, as the details presently to be given will show. If I were to go through such work again, I should try to reduce the importance of temperature changes in the copper connecting wires by increasing the resistance of the spirals or the change of temperature of the stream between them.

Heating and Flow of Water.

The method of heating and controlling the flow of the streams of water has been described in previous papers. The only feature of importance

to add to the description is this, — that in these later experiments the freedom of movement of the covers of the gas-holders, upon which the accuracy of regulation of the gas pressure depends, has been greatly increased by keeping the hammer of an electric bell in brisk action against the side of each gas-holder. When the regulating devices were working well the maximum variation of temperature in either stream during one of the main sets of observations, occupying some 45 minutes, was usually about one fifth of a degree C.

Results in Detail for Thermal Conductivity.

Experiments on conductivity of the iron with the apparatus as described in this paper were begun July 13, 1899. The results of that day and of July 14 are not here given, as they were obtained before the full importance of some precautions was recognized; but all the results obtained later are recorded below. The subscript 1 refers to cases in which the warmer stream of water ran above the disk, the subscript 2 to those in which it ran beneath the disk. T, the mean of T_1 and T_2, is the mean temperature of the disk during a pair of complementary trials. K, the mean of K_1 and K_2, is the mean value of the conductivity given by a pair of complementary trials. The results obtained July 31 and August 2 are distinguished from the others by the fact that they were made after a certain change in the position of the thermo-metric spirals (see p. 135).

Date	T_1	T_2	K_1	K_2	T	K	
July 17, '99	29°.2	28°.9	0.1521	0.1531	29°.1	0.1526	
" 18, "	28°.7	28°.5	0.1468	0.1553	28°.6	0.1511	
" 22, "	28°.2	28°.1	0.1568	0.1500	28°.2	0.1534	0.1528
" " "	28°.1	27°.8	0.1539	0.1513	28°.0	0.1526	
" 27, "	27°.4	27°.5	0.1580	0.1510	27°.5	0.1545	
" 31, "	27°.7	27°.4	0.1465	0.1529	27°.6	0.1497	0.1528
Aug. 2, "	28°.3	28°.2	0.1543	0.1573	28°.3	0.1558	
			0.1526	0.1530	28°.2	0.1528	
July 18, "	58°.8	58°.6	0.1531	0.1529	58°.7	0.1530	
" 22, "	58°.9	58°.8	0.1608	0.1441	58°.9	0.1525	0.1521
" " "	58°.6	58°.7	0.1593	0.1420	58°.7	0.1507	
" 27, "	56°.2	57°.6	0.1552	0.1490	56°.9	0.1521	
" 31, "	57°.8	57°.7	0.1510	0.1498	57°.8	0.1504	0.1502
Aug. 2, "	58°.3	58°.6	0.1568	0.1432	58°.5	0.1500	
			0.1560	0.1468	58°.3	0.1514	

The values of K given above take no account of the variation in the specific heat of water between 28°.2 and 58°.3. The temperature coefficient of K obtained from the trials made July 31 and August 2 after a change in the arrangement of the spirals, which change was supposed to make for greater accuracy of results, is decidedly greater than that obtained from the trials which preceded this change; but the considerable difference between the values of K at low temperature found July 31 and August 2 makes it unsafe to give especial weight to the value of the temperature coefficient calculated from the trials of these two days. The best course appears to be to take the mean of all the results at low temperature and compare it with the mean of all those at high temperature; and this has been done, with the result stated at the beginning of this paper.

Measurement of the Electrical Resistance.

A satisfactory determination of the mean electrical resistance of the iron was a work of considerable difficulty. I attempted it at first by use of several little cylinders, each taken singly, such as had been used in testing the thermo-electric quality of the iron (see p. 128). I found, however, that the last milling which these cylinders had been subjected to had left them somewhat irregular in diameter, so that it was impossible to measure this dimension accurately, even when calipers with jaws meeting along a narrow line were used. Accordingly I used the somewhat larger cylinders, already mentioned, which had suffered much less from the imperfections of the milling process. These were about 0.23 cm. in diameter, and could be measured with satisfactory accuracy.

The straight thick wire of a Carey Foster bridge having been replaced by two stout brass rods lying in line, with a gap between their ends, which were amalgamated, one of the iron cylinders was placed end to end between these rods and firmly held there under considerable pressure. Then the resistance of a certain measured length, 1.472 cm., of the iron bar was determined in the usual way by means of the bridge and the accompanying low resistance coils. Four cylinders were tested in this way, and their mean specific resistance was found to be 12430, C. G. S., at 22° C.

Later the resistance of the same length of each of these bars and of five other similar bars, held as just described, was measured by a potentiometer method, the potentiometer wire being of copper drawn especially for this test. The mean specific resistance of the nine bars, as found by this latter method, was 12240, C. G. S., at 18° C., the value given in the beginning of this paper.

Appendix.

Does the conductive action of the copper wires attached to the platinum thermometer spirals introduce error by preventing these spirals from taking the temperature of the water flowing past them?

If the warming or cooling produced by the action of the copper wires were equally great at the two spirals, no harm would result, as it would not affect the difference of their temperatures, which is the quantity measured; but this perfect compensation can hardly be, for all of the copper connections are subjected to very nearly the same temperature conditions outside the supporting hard rubber plugs, while the spirals themselves differ in temperature about 0°.5. The differential effect, upon which alone the possibility of sensible error depends, is very much the same as if one of the spirals were at the same temperature as its connecting wires outside the plug and the other spiral 0°.5 warmer or colder than its connecting wires outside the plug. It is possible to make a very rough estimation of the maximum amount of error which could arise from such a condition. For the purpose of this calculation it may be assumed that the hard rubber plug is a non-conductor of heat, — an assumption which tends to magnify the effect under discussion. The length of the plug, that is, the length of the wire from air to water, is 2.5 cm., the diameter of the wire about 0.1 cm., the length of each copper wire exposed to the water about 1.6 cm. The length of the platinum wire in each spiral is about 22 cm., and its diameter about 0.012 cm. The point of attachment of the platinum to the copper is near the middle of the part of the copper exposed to the water. We will discuss the action of a single copper wire, and assume that one half of the platinum wire was attached to this by one end, the other end being free. For this purpose it will be necessary to know something about the "surface conductivity" of copper immersed in running water. Fortunately the main experiment with the copper-coated disk gives us some information in regard to this, — very inaccurate information, no doubt, but sufficient for the present purpose.

In this main experiment, with a mean temperature t in the disk, and with a temperature $t + 4$ in the stream on one face and $t - 4$ in the stream on the other face, the two meeting surfaces of copper and iron had respectively temperatures about $t + 0.8$ and $t - 0.8$, we will say. Assuming the thermal conductivity of copper to be eight times that of iron, and remembering that the copper coatings are each 0.2 cm. thick while the disk is 2 cm. thick, we get for the temperatures of the two outer

copper surfaces, in contact with the water, the temperatures $t + 0.82$ and $t - 0.82$ respectively. This makes each copper coating to have a temperature gradient of $0^\circ.1$ per cm., with a difference of $3^\circ.18$ between its outer surface and the water stream flowing across it. The ratio of the temperature gradient to the external difference is therefore about $\frac{1}{32}$.

According to this we may infer that a stream of water flowing across one face of a copper wire, with a speed equal to that of the flow across the surface of our disk, and with a temperature t degrees above the temperature of the face of the wire, will maintain within that wire a gradient of temperature equal to $t \div 32$, all lateral action being excluded.

The point of attachment of the platinum wire to the copper is about midway of the exposed part of the copper, and is as much as 3.0 cm. from the outer end of the plug. If the copper wire terminated at this point of attachment, and suffered conductive contact with the water only at its terminal surface, the change of temperature from the outer end of the plug, supposed non-conductive, to the end of the wire would accordingly be about $\frac{3}{32}$, $\frac{1}{11}$, as great as the difference of temperature between the end of the wire and the water flowing past it. If, therefore, the wire at the outer end of the plug exceeds in temperature the stream of water by $0^\circ.5$, as we will assume, the fall of temperature within the wire would be about $0^\circ.04$, and the end of the wire would be about $0^\circ.46$ above the temperature of the stream. This conclusion, however, is based on a false assumption as to the area of contact of the wire with the water; in fact, this area of contact is about sixty times as great as the cross-section of the wire, and the point of attachment of the platinum is near the middle of this area, so that we shall not be very far from the truth in assuming that the temperature of the copper at the cross-section next the point of attachment of the platinum is the same that it would be if the wire had contact with the water only at this cross-section but had sixty times as great a surface conductivity as such an area really has in contact with the stream. This leads to the conclusion that the fall of temperature within the wire, from the outer end of the plug to the point of attachment of the platinum, is about $\frac{60}{11}$ times as great as the difference of temperature between the point of attachment and the stream. This last difference would therefore be rather less than $0^\circ.1$, but we will call it that.

The problem now is to find how much the mean temperature of a platinum wire 0.012 cm. in diameter and 11 cm. long will exceed that of the water stream in which it is placed, if one end of this wire is kept $0^\circ.1$ above the temperature of the water. This problem is of a familiar sort,

and is easily dealt with if we know the ratio between the thermal conductivity, K, of the platinum and its "surface emissivity," E, in the stream of water. Assuming E to be the same for platinum as for copper, and K to be $\frac{1}{8}$ as great for platinum as for copper, we get for $E \div A$ the value $\frac{1}{4}$. We now have (see Preston's "Heat," p. 513)

$$\mu^2 = \frac{E\,p}{K\,A} = \frac{1}{4} \times \frac{.012}{.006^2} = 83,$$

or $\mu = 9$ in round numbers. Then, using the formula $\theta = \theta_0\,\epsilon^{-\mu x}$, where θ_0 is excess of temperature of the heated end of wire above temperature of water, θ the excess of temperature at any point distant x cm. from this end, and ϵ the Napierian base, we have, reckoning θ in per cents of a degree: —

x	θ		
0	10		
		>7.1	
0.1 cm.	4.1		
		>2.8	
0.2 "	1.7		Mean
		>1.2	
0.3 "	0.7		2.4 % of 1°
		>0.5	
0.4 "	0.28		
		>0.2	
0.5 "	0.11		

Accordingly the mean excess of temperature of the wire along its first 0.5 cm., less than $\frac{1}{20}$ of its whole length, would be about 5 % of the usual difference of temperature, about 0°.5, between the two spirals; and beyond this point the excess would be very small; so that the error made by neglecting the difference of temperature between the spirals and the water is not important, provided the calculation just made is tolerably accurate. The most uncertain element in this calculation is probably the value of the "surface emissivity," which is based on observations made on the behavior of the disk and the streams across its face. But as the velocity of the water in passing the spirals is probably ten times as great as its mean velocity across the disk, it seems altogether likely that a sufficiently low estimate of emissivity has been used in the calculation, and that the possible error from the source in question has been overestimated in the discussion just given.

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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

A NEW CONCEPTION OF THERMAL PRESSURE AND A THEORY OF SOLUTIONS.

By Gilbert Newton Lewis.

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Introduction.

For an understanding of all kinds of physico-chemical equilibrium a further insight is necessary into the nature of the conditions which exist in the interior of any homogeneous phase. It will be the aim of the present paper to study this problem in the light of a new theory, which, although opposed to some ideas which are now accepted as correct, yet recommends itself by its simplicity and by its ability to explain several important phenomena which have hitherto received no satisfactory explanation.

The theory suggested itself in the consideration of certain remarkable general laws which treat of heterogeneous equilibrium in which the several phases are subject to different pressures. These laws will be discussed in the first section of this paper, and in the second section it will be shown that they can all be explained by a single simple assumption. In the third section it will be shown that the same assumption is alone sufficient to explain all the laws of dilute solutions. In the last section other consequences of the new theory will be discussed, especially in their relation to the theory of van der Waals.

I.

The Effect of Pressure on the Tendency to Pass from Phase to Phase.

It has been shown by several investigators * that, in a number of cases of heterogeneous equilibrium, if the pressure upon one of the phases alone is changed, a readjustment takes place that can be easily calculated.

* Poynting, Phil. Mag. (5), XII. 32 (1881); Schiller, Wied. Ann., LIII. 396, (1894); Hall, Jour. of Phys. Chem., III. 452 (1899.)

In order to introduce a general discussion of this problem, which leads to very notable and instructive results, let us consider first a simple, special case, namely, the question of the effect upon the vapor pressure of a liquid caused by a change in the total pressure on the surface of the liquid.

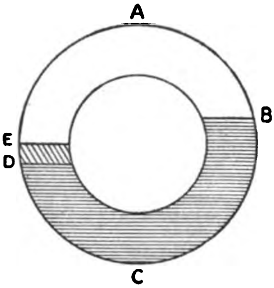

FIGURE 1.

Figure 1 represents a ring-shaped enclosure containing a liquid X in the part B C D, and the vapor of X throughout the remaining space. The space D E contains also an infinitesimal layer of some inert and insoluble gas, which is prevented from diffusing into the space B A E by a membrane at E, which is permeable only to the vapor of X. The foreign gas thus enclosed exerts a pressure upon the liquid at D and maintains a difference of level, dH, between B and D *. This pressure, moreover, must have an effect upon the vapor pressure of the liquid, for, on account of its weight, the pressure of the vapor is greater at D than at B, but the liquid is in equilibrium with the vapor at both points, therefore the vapor pressure of the liquid is greater at D than at B. If dP_1 represent the difference in vapor pressure between B and D, and s_1 the specific gravity of the vapor, then we may write,

$$dP_1 = s_1\, dH.$$

If dP_2 represent the difference in the total pressure upon the liquid at B and D, and s_2 the specific gravity of the liquid, then

$$dP_2 = s_2\, dH.$$

From these two equations,

$$\frac{dP_1}{dP_2} = \frac{s_1}{s_2},$$

or if σ_1 and σ_2 represent the specific volumes of vapor and liquid respectively, then

$$\frac{dP_1}{dP_2} = \frac{\sigma_2}{\sigma_1}. \tag{1}$$

* Objection has been raised to proofs of this kind; thus, in this case, it would be argued that in reality the liquid will distil from B to the space above E. That this may happen in no way invalidates the proof, for it is not necessary that it should happen. By keeping E A free from drops of the liquid the system is in perfect equilibrium, the equilibrium of supersaturation. That there is another more stable equilibrium possible is of no concern.

In general, therefore, an increase in the total pressure upon a liquid will cause an increase in the vapor pressure, and the ratio of the two changes will be the ratio of the specific gravities of liquid and vapor. This relation, which has been stated before in several different forms, has an importance which has been hitherto overlooked, probably because, under ordinary circumstances, the calculated effect upon the vapor pressure has been too small to be measurable, and also because the result has usually been obtained by assuming the applicability of the gas law to the vapor, thus making the result seem only an approximation.

Although ordinarily the magnitude of the effect is extremely small, in some cases it must be of considerable significance. Equation (1) shows that the influence of external pressure upon the vapor pressure depends upon the relative densities of vapor and liquid. Therefore, for liquids of high molecular weight, as a rule, the effect will be considerable, and also in the case of a liquid whose vapor is under high pressure. But especially must the effect be considered in the study of critical phenomena and the influence of foreign substances in the determination of the critical constants, for in the region about the critical point the densities of liquid and vapor approach identity. The proof of equation (1) given above shows that its validity rests upon no assumption as to the specific nature of the two phases considered. The probability is immediately suggested that equation (1) is simply a special statement of a general law applying to all heterogeneous equilibrium. That this is true may be shown in the following way.

In figure 2, let A B C and A′ B′ C′ represent two similar enclosures. In the first, X_1 and X_2 are two different phases of a simple substance X; P_1 and P_2 are the pressures exerted by an inert gas on the two sides and are such that equilibrium exists; B is a membrane permeable only to the vapor of X. The specific volumes in phases X_1 and X_2 are σ_1 and σ_2 respectively. The enclosure A′ B′ C′ is the same as A B C except that here there is another state of equilibrium in which the pressures upon the phases X_1 and X_2 are $P_1 + dP_1$ and $P_2 + dP_2$, and the specific volumes are $\sigma_1 - d\sigma_1$ and $\sigma_2 - d\sigma_2$ respectively.

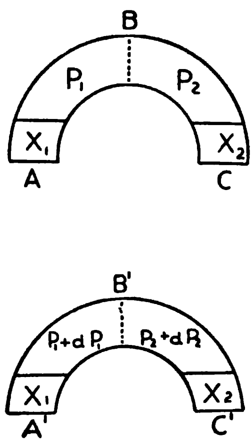

FIGURE 2.

Now let the following process occur reversibly and isothermally: (1) One gram of X_1 is

removed from A at pressure P_1; (2) it is compressed to $P_1 + dP_1$; (3) it is introduced into the second enclosure at A′ against pressure $P_1 + dP_1$; (4) one gram of X_2 is taken from the second enclosure at C′ at pressure $P_2 + dP_2$; (5) it is allowed to expand to P_2; (6) it is introduced into the first enclosure at C against pressure P_2.

The system will have returned now by internal adjustment to its original condition. The quantities of work done by the system in the several steps are,

$$W_1 = P_1 \sigma_1,$$
$$W_2 = - P_1 d\sigma_1,$$
$$W_3 = - (P_1 + dP_1)(\sigma_1 - d\sigma_1),$$
$$W_4 = (P_2 + dP_2)(\sigma_2 - d\sigma_2),$$
$$W_5 = P_2 d\sigma_2,$$
$$W_6 = - P_2 \sigma_2,$$

By writing the sum of these terms equal to zero, according to the second law of thermodynamics, we obtain the equation,

$$\sigma_2 dP_2 - \sigma_1 dP_1 = 0; \quad \text{or,} \quad \frac{dP_2}{dP_1} = \frac{\sigma_1}{\sigma_2}. \tag{2}$$

The meaning of this equation is obvious. When under any conditions two phases of a substance are in equilibrium and the pressure is increased upon one phase, then in order to maintain equilibrium the pressure must be increased on the second phase; and the second change in pressure must be to the first as the specific volume of the first phase is to that of the second. For example, if ice and water are in equilibrium at atmospheric pressure and an additional pressure of one atmosphere is put upon the ice alone, then equilibrium can be maintained by an additional pressure of 1.09 atmospheres upon the water, since 1.09 is the ratio of the volumes of ice and water.

The above law has been derived without any assumption whatever, and is based only upon the second law of thermodynamics. It must be considered, therefore, in the same degree as the latter a universal and exact law of nature. This law may be presented in another form.

There is a tendency for the particles of every phase to escape into some other phase. Later a function ψ will be so defined as to represent this *escaping tendency.* Here it will be sufficient to consider ψ merely a quantity such that when two phases are in equilibrium, ψ has the same value in both; when not in equilibrium, ψ is greater in the less stable

phase. When two phases in equilibrium are subjected to infinitesimal changes of pressure resulting in a second state of equilibrium,

$$d\psi_1 = d\psi_2, \text{ or in other terms, } \frac{\partial \psi_1}{\partial P_1} d P_1 = \frac{\partial \psi_2}{\partial P_2} d P_2,$$

where ∂ denotes a partial differential; finally,

$$\frac{\frac{\partial \psi_1}{\partial P_1}}{\frac{\partial \psi_2}{\partial P_2}} = \frac{d P_2}{d P_1} = \frac{\sigma_1}{\sigma_2},$$

from equation (2). In general, therefore,

$$\frac{\partial \psi}{\partial P} = \kappa \sigma, \tag{3}$$

where κ is a constant.

That is, *the change in the escaping tendency of any phase with a given change in the external pressure is proportional to the specific volume of the phase.* For example, if solid and liquid benzol are in equilibrium at one pressure and this pressure is increased, the escaping tendency of the liquid is increased more than that of the solid in the ratio of the specific volumes, 1.13 to 1.11. The liquid phase, therefore, totally disappears. In the case of water, whose liquid is denser than the solid, the phenomenon is exactly reversed. The above law, therefore, expresses quantitatively what the principle of Le Chatelier states qualitatively.

In the preceding discussions we have dealt with different phases of a simple substance, not with a mixture, but the same method of proof and therefore the same law can be shown to be applicable to all cases in which the phases considered are all capable of being converted entirely, under the conditions of equilibrium which exist,* into one substance, whether this be a pure substance or a mixture.

Equations (1), (2), and (3) apply, therefore, to all cases where there is association, dissociation, polymerization, or isomerization, provided that all these different molecular species are in "true" equilibrium with one another.

* This qualifying phrase is necessary. The different phases must not merely have the same composition. Thus, a system composed of water and a gaseous phase of hydrogen and oxygen in equivalent proportions differs essentially from a system of solid ammonic sulphydrate and a gaseous phase containing ammonia and hydrogen sulphide in equivalent proportions. The latter is subject to the above treatment, the former is not.

For the sake of completeness the corresponding phenomena in the case of other mixtures will next be considered.

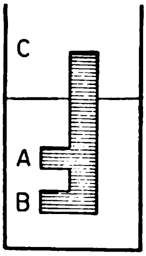

FIGURE 3.

In Figure 3 let the tube C A B contain a homogeneous mixture of liquids and the outer vessel one of the pure liquids, X, alone. A and B represent two membranes permeable to X alone. If pressure is applied in the tube so that X neither enters nor leaves the tube at A, then there will be equilibrium at B also, for otherwise a continuous cyclic process would be kept up, contrary to the second law of thermodynamics. The escaping tendency of X is the same outside and inside at A and also at B, since there is equilibrium at both points, but the changes in pressure between A and B which determine the magnitude of that tendency are different inside and outside the tube. If dH is the height A B, and the specific gravity of the mixture and the liquid X are S_1 and S_2 respectively, the changes in pressure are $S_1 dH$ inside the tube and $S_2 dH$ outside. If dP_1 and dP_2, respectively, represent these changes in pressure,

$$\frac{dP_1}{dP_2} = \frac{S_1}{S_2}; \quad \text{or} \quad \frac{dP_1}{dP_2} = \frac{\sigma_2}{\sigma_1}.$$

This is the same as equation (2), and at first sight it seems that the influence of pressure upon the equilibrium between two phases is as simple in the case of mixtures as in the case of pure substances. It is actually, however, much more complicated. In the above example there is a change in the escaping tendency of X from the mixture, not only because there is a change of pressure, but also because, in general, between A and B there is a change in the relative amounts of the components of the mixture. In other words, the concentration of X differs at A and B.* Moreover if there is chemical equilibrium in the mixture the chemical reaction will have run nearer to completion in A or in B according to whether the total volume is increased or diminished by the reaction. On account of this complexity the further study of mixtures, although of much interest, must be deferred, since it is not essential to the present paper.

* See Gouy and Chaperon, Ann. Ch. Ph. (6), XII. 384 (1887).

II.

Thermal Pressure.

When we consider again the laws which govern different phases of a simple substance, as expressed in equations (1), (2), and (3), their great simplicity and generality suggest that some equally simple physical explanation is possible. As we have already seen, an increase in the external pressure always produces an increase in the tendency of a substance to escape from any phase. The pressure can influence this tendency only by changing the conditions within the phase. Let us briefly analyze these conditions.

If in the interior of any homogeneous phase of infinite extent, not subject to gravity, we imagine a septum of infinitesimal thickness, i. e. a mathematical plane, there is every reason to believe that upon each side of this septum there would be a pressure exerted which would depend upon the temperature, and would in general differ from the pressure observed at the surface of the phase. This internal pressure will be termed the *thermal pressure* of the phase. It would be expressed, in the hypothetical terms of the kinetic theory, as equal to the number of molecules passing from one side to the other in unit time through an imaginary plane of unit area, multiplied by twice the average momentum of each molecule in the direction perpendicular to the plane.

An illustration of the meaning of thermal pressure is the quantity $\frac{R\,T}{v - b}$ in the equation of van der Waals; this quantity, if the theory of van der Waals is correct, represents the thermal pressure of a compressed gas. Thermal pressure will denote the pressure due to heat in distinction from that due to attractive or repulsive forces.

The actual pressure observed at the surface of the phase may be considered equal to the thermal pressure plus or minus the resultant of all other repulsive or attractive forces acting in the phase. This resultant will be called the *attractive pressure* and designated by a, — positive if an attractive force, negative if repulsive. If the thermal pressure is represented by β we have the equation,

$$\beta - a = P, \tag{4}$$

where P is the external pressure. This equation combined with equation (3) gives,

$$\frac{d\psi}{d\,(\beta - a)} = \kappa\,\sigma, \tag{5}$$

that is, the tendency of a substance to escape from a phase is greater, the greater the thermal pressure and the less the attractive pressure. Now equation (5) applies to any phase of any pure substance, solid, liquid, or gaseous. In some cases a small change in pressure will cause a very great change in both β and α; in others, a very small change in both. The change in β relative to that in α will sometimes be very great, sometimes very small. In general, the function ψ depends, not upon the absolute, individual magnitudes of β and α, but only upon their difference; and we may conclude from the very universality of equation (5) that it is true not merely when β and α are changed by a change in the external pressure, but that in general a change in β or α, no matter how caused, will affect the quantity ψ only as it changes their difference $\beta - \alpha$, and that any change in β accompanied by an equal change in α has no effect on ψ since one neutralizes the other. This will be a necessary postulate in the development of the following theory.

Let us consider a system composed of a liquid or solid phase and its vapor, under such circumstances that the latter obeys the laws of a perfect gas. By equation (1), if we replace $\frac{\sigma_2}{\sigma_1}$ by $\frac{v_2}{v_1}$, the molecular volumes, and write $v_1 = \frac{RT}{P_1}$ where R is the gas constant, T the absolute temperature, we obtain

$$\frac{dP_1}{dP_2} = \frac{v_2}{v_1}; \text{ or, } \frac{dP_1}{dP_2} = \frac{P_1 v_2}{RT}; \text{ or, } \frac{dP_1}{P_1} = \frac{dP_2}{\left(\frac{RT}{v_2}\right)}. \qquad (6)$$

This equation expresses the very remarkable result that the change in vapor pressure is to the total vapor pressure as the change in the external pressure upon the solid or liquid phase is to the pressure which that phase would exert if it should behave as a perfect gas. This may be presented in different form by the aid of equation (4) as,

$$\frac{dP_1}{P_1} = \frac{d(\beta_2 - \alpha_2)}{\left(\frac{RT}{v_2}\right)}. \qquad (7)$$

In attempting an explanation of these relations let us consider first a case in which the change in α_2 is negligible compared with the change in β_2. That is, β_2 changes while α_2 remains constant. Since the attractive forces remain constant, it might be predicted *a priori* that the vapor pressure would be proportional to β_2, the thermal pressure, especially if the kinetic point of view is adopted; for the vapor pressure is believed to be

dependent upon the chance of any one molecule to escape from the phase in question and upon the number of molecules per second which share this chance. This chance for each molecule will depend (1) upon its momentum and (2) upon the various influences that retard its motion outward. The latter are the various attractive forces that have been included in the quantity a_2. Therefore in any isothermal change in which a_2 is constant neither the momentum * nor the retarding influences vary, and the vapor pressure then will be proportional to the number of molecules coming to the surface per second, and therefore proportional to the thermal pressure. Hence,

$$P_1 = k\,\beta_2\,;\ \text{or,}\ \frac{d\,P_1}{P_1} = \frac{d\,\beta_2}{\beta_2}. \tag{8}$$

Moreover in the general case, when both β_2 and a_2 change, if we postulate, as on page 152, that equal changes in β_2 and a_2 produce equal and opposite effects on the vapor pressure, then we should expect that the change in vapor pressure would be to the total vapor pressure as the *effective* change in thermal pressure is to the total thermal pressure; if "effective change" in β_2 is used to mean the change in β_2 over and above that required to compensate for change in a_2. That is,

$$\frac{d\,P_1}{P_1} = \frac{d\,(\beta_2 - a_2)}{\beta_2}. \tag{9}$$

Comparing this equation, derived from kinetic considerations, with the one which has been proved thermodynamically, namely, equation (7),

$$\frac{d\,P_1}{P_1} = \frac{d\,(\beta_2 - a_2)}{\left(\frac{R\,T}{v_2}\right)},$$

it is evident that the only assumption necessary to make the two identical is the following: *The thermal pressure of any phase is equal to the pressure which the substance would exert if, under the same conditions, it should behave as a perfect gas.*

Objection to this assumption cannot be made on the ground that it is not sufficiently simple; but is it too simple? What has become of the correction "b" of van der Waals, to say nothing of all the complications that may exist in a liquid or solid phase? It must be confessed that the above assumption seems, at first sight, absurdly simple and quite improbable. I shall attempt to show, however, that this assumption is not only

* Whether this momentum is quite constant will be considered later.

not opposed to any facts, but is capable of explaining many facts besides those which we have already discussed. On the other hand, this assumption seems entirely irreconcilable with one of the accepted principles of the kinetic theory, but it is directly deducible from this theory if the latter is modified in the way which will now be proposed.

In the kinetic theory of gases there are two quantities of fundamental importance: one is the kinetic energy of a molecule, and is represented by $\frac{1}{2} mu^2$, where m is the mass, and u the velocity of the molecule; the other is that which has been called thermal pressure, and is proportional to $mu \times n$, the product of mu, the momentum of the molecule and n, the number of molecules whose centres of gravity pass in one second through unit area. In the perfect gas n is proportional to u; the kinetic energy and the thermal pressure in a perfect gas are proportional to each other and to mu^2. In substances, however, which deviate from the condition of a perfect gas the kinetic energy will still be proportional to mu^2, but $(mu)\,n$ will be proportional to mu^2 only when n is proportional to u, and this will be the case only when the molecules behave on collision as perfectly elastic mathematical particles, that is, when there is no correction corresponding to the quantity b of van der Waals.

In the kinetic theory of gases the temperature is shown to be measured by mu^2, and in every attempt hitherto to extend this theory to less simple conditions of matter the fundamental assumption has been that the kinetic energy of progression of the molecule is proportional to the absolute temperature. I now propose to reject this assumption entirely, and to substitute the assumption that the temperature is in all cases measured by the quantity $(mu)\,n$ or by the thermal pressure; more explicitly, instead of assuming that the kinetic energy of a molecule of any substance is the same as if it were a perfect gas, while the quantity $(mu)n$ may vary in any way, it will now be assumed that $(mu)\,n$ in any substance is the same as it would be if the substance should behave as a perfect gas and that at one temperature the average kinetic energy of progression of the molecule may vary.

This proposition appears less revolutionary if it is borne in mind that in the only case in which the kinetic theory is entirely satisfactory, namely, the perfect gas, the two assumptions become identical, and, therefore, the change in no way affects the previous kinetic explanation of all the phenomena of gases. The only other application of the kinetic theory that has met with any degree of success, the equation of van der Waals, will be discussed later in its relation to this new kinetic conception.

In the meantime it is necessary to consider what advantage in theory may be gained by adopting the proposed assumption. According as we deal with a pure substance or a mixture, the quantity $(mu)\,n$ will be a measure of the total thermal pressure, or of the partial thermal pressure of any one molecular species, if we so designate that pressure which may be conceived to be exerted on either side of an infinitesimally thick membrane in the interior of a homogeneous phase by the molecules of that particular molecular species. The principle of thermal pressure offered on page 153 may be put in the form of an equation, as,

$$\beta = \frac{n\,R\,T}{V}, \tag{10}$$

where β is the partial or total thermal pressure, as the case may be, of some one molecular species; n is the number of gram molecules of this species; R is the gas constant; T, the absolute temperature; and V, the total volume occupied.

This idea could be otherwise expressed by an extension of the rule of Avogadro, as follows: *All substances at the same temperature and the same thermal pressure have the same number of molecules in unit volume.*

Equation (10), which, if correct, represents a universal principle of nature, must be capable of very wide application. In the next section it will be shown that by assuming the correctness of this equation, and without any other hypothesis, it is possible to derive all the laws of dilute solutions. It is well to emphasize that while equation (10) was shown to be consistent with the kinetic theory in order that it might appear more probable, still, having once assumed this equation, it is unnecessary henceforth to adopt any kinetic view whatever.

III.

A Theory of Solutions.

Notwithstanding the simplicity of the phenomena of solutions, they have as yet received no entirely adequate explanation. In fact, in some explanations assumptions have been necessary that are inherently improbable. In the theory of solutions here presented it will be unnecessary to assume either that the solute does or does not combine chemically with the solvent in any way. It will only be necessary to suppose that when n gram molecules of any substance are dissolved in a solvent, that

in the solution there are still n gram molecules of something different from the solvent itself.*

All the general laws of solutions may be derived thermodynamically from either of two empirical equations, each of which, moreover, may be derived from the other. The first is the law of van 't Hoff,

$$\Pi = \frac{n R T}{V}, \tag{11}$$

where Π is the osmotic pressure of a solution containing n gram molecules of a solute in a volume V.

The second may be written,

$$\frac{\psi_1 - \psi_2}{\psi_1} = \frac{n}{n + m}, \tag{12 a}$$

or, more strictly,

$$\frac{d\psi}{\psi} = \frac{dn}{m}. \tag{12 b}$$

In (12 a) n and m represent the number of gram molecules of solute and solvent respectively; ψ_1 and ψ_2 denote the escaping tendencies of the solvent from the pure solvent and the solution respectively; in (12 b) $d\psi$ represents the change in the escaping tendency of the solvent, due to dn gram molecules of the solute. In order to make the equations entirely definite it is necessary to give the function ψ, or the escaping tendency, a meaning less vague than that which sufficed on page 148, by defining the actual value of ψ for some one condition of each substance. Therefore the escaping tendency of a perfect gas will be defined as equal to its gas pressure, and the escaping tendency from most actual gaseous phases will be approximately the partial gas pressure.

Equation (12 b) simply unites in one general equation the law of Raoult for the lowering of vapor pressure, the law of Nernst for the lowering of solubility, and less directly the law for the depression of the

* It is probable that, in some cases, "association" with the solvent takes place and in others that it does not. A crystal containing water of crystallization seems in no way different from any other double salt, and since it has often been shown that double salts exist as such in solution, it is probable that water enters into many molecular compounds in solution. Thus it seems probable that when a salt forms a number of solid hydrates, all these compounds and others whose solubility is greater are present in solution in proportions varying continuously with concentration and temperature. On the other hand, it is extremely unlikely that when a substance like hydrogen gas dissolves in water a chemical combination of any kind takes place.

freezing point. It may be stated in words thus: The "relative" diminution in the escaping tendency of the solvent upon the addition of an infinitesimal amount of a solute is equal to the ratio of the number of gram molecules of solute and solvent. It is probable that equation (12 b), besides being more general than the equation of Raoult, is also more accurate; for it will appear likely from the theory here developed that Raoult's law is exact only when the vapor of the solvent follows the gas law, but that equation (12 b) represents a universal law.

Our problem is now to show that equations (11) and (12) are directly deducible from the idea of thermal pressure contained in equation (10). Since the reasoning would be the same whether our goal is the general equation (12) or the special form of Raoult, for the sake of concreteness it will be convenient to develop first the latter equation, and in the simple case of a solution in a solvent to whose vapor the gas law may be applied. Let us determine theoretically in this case the influence of the solute on the vapor pressure of the solvent. This effect may be divided into two which are entirely independent; the first is the effect of the thermal pressure of the solute on the condition of the solvent (this may be pictured kinetically as the influence of the mere motion of the solute molecules); the second is the effect of the attraction or repulsion of the solute for the particles of the solvent. It will therefore simplify the discussion if we study these two influences separately, beginning with the latter.

In a hypothetical case in which we may imagine the particles of the solute to be evenly distributed through a solution, and to have no effect except by an attraction for the solvent particles, the only practical effect of the presence of the solute will be to increase the attractive pressure of the solvent inward. Then, in order to maintain equilibrium, according to equation (4),

$$P = \beta - \alpha,$$

since the external pressure is unchanged, the total volume will decrease on account of the new attraction until the thermal pressure of the solvent is increased by the same amount as the attractive pressure, and we may write, therefore,

$$d\beta = d\alpha; \quad \text{or,} \quad d\beta - d\alpha = 0.$$

Comparing this with equation (5) or equation (7), it is evident that *the attraction of solute for solvent is not the cause of the lowering of vapor pressure in a solution*, and that a mere attraction or repulsion between the solvent and solute does not change the vapor pressure of the solvent,

because the change in the attractive pressure is always compensated by an equal change in the thermal pressure, and these two changes produce equal and opposite effects upon the vapor pressure. This conclusion will simplify the discussion of the second influence of the solute, the effect of thermal pressure; for since the attraction or repulsion of solute for solvent is without effect, we may consider with perfect generality the case in which this attraction or repulsion is zero. In such a case, if β and a represent the thermal and attractive pressures of the pure solvent, when the solute is added in general a change in volume occurs in which β and a change to $\beta + d\beta$ and $a + da$. The total attractive pressure of the solution is $a + da$; but the total thermal pressure of the solution includes the partial thermal pressure of the solute, which may be designated by $d\beta'$. The equation of the solution is, then,

$$P = (\beta + d\beta + d\beta') - (a + da). \tag{13}$$

Combining this with the equation of the pure solvent,

$$P = \beta - a,$$

we obtain

$$d\beta - da = -d\beta'. \tag{14}$$

Now the vapor pressure depends on the attractive pressure and the thermal pressure of the solvent alone, in accordance with equation (7), which may be written,

$$\frac{dP_1}{P_1} = \frac{d(\beta - a)}{\frac{mRT}{V}}.$$

Substituting equation (14) and writing from equation (10),

$$d\beta' = \frac{(dn)\ RT}{V},$$

we obtain,

$$\frac{dP_1}{P_1} = -\frac{\frac{(dn)\ RT}{V}}{\frac{mRT}{V}} = -\frac{dn}{m},$$

dP_1 being negative for a decrease in P_1. This is a statement of the law of Raoult, which is thus shown to be a direct consequence of the principle of thermal pressure expressed in equation (10). Perhaps a more intimate understanding of the way in which the thermal pressure of the solute affects the vapor pressure of the solvent may be obtained from another point of view which affords a simple but somewhat less rigorous demonstration.

In any pure solvent, according to equation (5), the tendency to escape into some other phase is dependent, not upon the actual values of the thermal and attractive pressures, but only upon their difference, which is the external pressure. At constant external pressure, therefore, the escaping tendency of the solvent is constant under all circumstances as long as the external pressure represents the difference between the thermal pressure of the solvent and the attractive pressure. If in a solution the thermal pressure of the solvent were equal to the total thermal pressure, the difference between this and the attractive pressure would be equal to the external pressure, and the escaping tendency would be the same as that of the pure solvent under the same external pressure. In reality the total thermal pressure is the sum of the partial thermal pressures of the solvent and solute; therefore, other things being equal, the escaping tendency should be to that of the pure solvent as the partial thermal pressure of the solvent is to the total thermal pressure. That is,

$$\frac{\psi_2}{\psi_1} = \frac{\beta}{\beta + \beta'},$$

where β is the partial thermal pressure of the solvent, β' that of the solute; but from equation (10),

$$\beta' = \frac{n\,R\,T}{V}; \quad \beta = \frac{m\,R\,T}{V}$$

therefore,

$$\frac{\psi_2}{\psi_1} = \frac{m}{m + n}.$$

From this equation,

$$\frac{\psi_1 - \psi_2}{\psi_1} = \frac{n}{m + n},$$

which is equation (12 a).

From this it appears that the lowering of vapor pressure, the lowering of solubility, and the lowering of the freezing point are all due to the fact that the solute shares with the solvent the support of the external and attractive pressure. Other things being equal, the greater the thermal pressure of the solute the less that of the solvent, and thus an increase in the amount of the solute diminishes the escaping tendency of the solvent, whether towards the gaseous phase, the solid phase, or another liquid.

An analogy may illustrate this explanation of Raoult's law, and at the same time introduce the consideration of osmotic pressure. If we consider m gram molecules of a gas A under a constant external pressure,

its tendency to escape is measured by that pressure. If n gram molecules of another gas B are now introduced, while the external pressure remains constant, the partial pressure of A is diminished by the fraction $\frac{n}{m+n}$ of its original value, and its escaping tendency will be diminished in the same ratio. Therefore gaseous solutions also obey equation (12), and in this case the explanation is obviously the one which has been given here for solutions in general.

If now we imagine the external pressure to be produced by the gas A outside, while within the pressure is borne by A and B, and if we imagine the outside and inside connected by a membrane permeable to A alone, then the gas A having a lower partial pressure inside will pass in from the outside, and equilibrium will not be established until the partial pressure of A is the same inside and outside; that is, until the total pressure inside is greater than that outside by the partial pressure of B. This is an exact analogy to the osmotic pressure in solutions, and in fact the same explanation can be given for both.*

Let us consider a solution and the pure solvent at the same external pressure originally, connected by a semipermeable membrane. The tendency to pass from solution to solvent is less than the tendency to pass from the solvent to solution, as we have seen. The solvent will therefore flow into the solution until, in some way, this tendency is balanced. Let us suppose that it is balanced by an increase in the external pressure on the solution. Then, since the function ψ of the solvent has been decreased by the thermal pressure of the solute, according to equation (14) it must be restored to its original value by an external pressure equal to that thermal pressure. In other words, the osmotic pressure of a dilute solution must be equal to the partial thermal pressure of the solute and,

$$\Pi = \frac{n\,R\,T}{V},$$

which is the law of van 't Hoff. This may be shown mathematically as follows: —

By generalizing equation (13) we obtain, as the equation of the solution, when the external pressure upon the solution is variable,

$$P + d\,P = \beta + d\,\beta + d\,\beta' - a - d\,a. \qquad (15)$$

* Since this paper was written an exactly similar statement of this analogy between the osmotic pressure and the pressure which a mixture of gases would show under the above conditions has been given by Ikeda, Zeit. Phys. Chem., XXXII. 280 (1900).

For the solvent,

$$P = \beta - \alpha.$$

Combining these we obtain,

$$dP = d\beta - d\alpha + d\beta'.$$

For equilibrium, when the escaping tendencies of the solution and solvent are the same,

$$d\beta - d\alpha = 0.$$

Hence the equation for osmotic equilibrium is,

$$dP = d\beta'.$$

But $dP = d\Pi$, the osmotic pressure, and

$$d\beta' = \frac{(dn) R T}{V},$$

from equation (10); hence

$$d\Pi = \frac{(dn) R T}{V},$$

the equation of van 't Hoff.

The conclusion that a certain osmotic pressure, and an equal change in the external pressure, together have no effect upon the tendency of a solvent to escape into some other phase may be verified in an interesting way.

In Figure 4 let A represent a pure liquid X; B, a solution in X, whose osmotic pressure is Π; C, the vapor of X; and D, an inert, insoluble gas exerting a pressure equal to Π. M and M′ are two membranes permeable to X alone. Since the gas pressure in D is equal to the osmotic pressure Π, X will not pass through the membrane M, therefore none of X will distil from solution to solvent or *vice versa*, for such a distillation would form a cyclic process contradicting the second law of thermodynamics. Hence the vapor pressure over a solution is the same as that over the pure solvent when the solution has an additional external pressure applied, equal to its osmotic pressure. The effect of the thermal pressure of a solute upon the vapor pressure of a solvent may be regarded, therefore, as due to a stress upon the surface of the solution acting like a diminution in external pressure of the same magnitude.

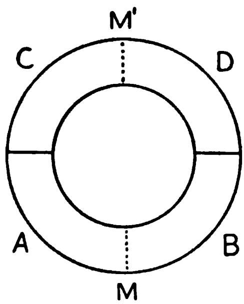

FIGURE 4.

IV.

If further investigation and further accordance with observed facts prove that the principle of thermal pressure, which has been here shown to possess a high degree of probability, is in fact an exact and universal law of nature, then there are few physico-chemical phenomena in which thermal pressure is not one of the most important determining factors; yet it would be premature to attempt at present any general application of the new theory. But there is one field in which the view here advocated is in direct conflict with a well-known and fruitful theory, — the theory of van der Waals. We shall, therefore, consider briefly the relations of thermal pressure to the equation of condition of liquids and gases and the van der Waals formula.

Equations (4) and (10) give at once a general equation of condition for all substances,

$$P = \frac{n\,R\,T}{V} - a, \quad \text{or} \quad P = \frac{R\,T}{v} - a, \tag{16}$$

where n is the total number of gram molecules in the volume V, and a, the attractive pressure, is the only quantity which is not immediately determined. It is probably, in most cases, a complicated function of volume and also of temperature.

Equation (16) is directly opposed to the theory of van der Waals, in that it does not recognize the influence upon the pressure of the so-called covolume, but, on the other hand, it in no way contradicts the validity of the equation of van der Waals considered as a purely empirical formula; for if that equation is regarded merely as a statement of experimental observation, it may be written as well in some other form. For example, instead of

$$P = \frac{R\,T}{v - b} - \frac{a}{v^2},$$

the second term might be expanded, and the equation written,

$$P = \frac{R\,T}{v} + R\,T\left(\frac{b}{v^2} + \frac{b^2}{v^3} + \frac{b^3}{v^4}\ \ldots\right) - \frac{a}{v^2}.$$

It would then be in the form of equation (16), in which

$$a = R\,T\left(\frac{b}{v^2} + \frac{b^2}{v^3} + \frac{b^3}{v^4}\ \ldots\right) - \frac{a}{v^2}.$$

This form of a would be of significance only in case the equation of van der Waals were perfectly accurate; as a matter of fact, no one has

claimed for it absolute accuracy, and it is probable that, except for its plausible theoretical basis, it would already have given place to a more accurate, purely empirical equation. If equation (16) is used in place of the formula of van der Waals as the equation of condition of gases and liquids, then the form of the function a must be found for each substance separately from its empirical equation; and on account of the presence of this function of unknown form, it is obviously impossible at present to test by experiment the validity of equation (16).

The curve of attractive pressure may be easily plotted in diagram on the PV plane. On this plane the rectangular hyperbola which, in the older theory, is only of ideal significance as the limit towards which the equation of condition tends as the substance approximates the perfect gas, in our present theory always represents a real physical quantity, — the thermal pressure. If from the ordinates of this hyperbola are subtracted the ordinates of the actual equation of condition, then, according to equation (4), these differences may be drawn as ordinates of the curve of attractive pressure. A general survey of many such curves will be necessary in order to show what general laws govern the variation of the quantity a. This task must be reserved for the future, but it may be confidently predicted that interesting and useful relations will be found which will give to equation (16) a specific value which it now lacks on account of its great generality; for the study of coincident conditions shows that from the behavior of one unassociated liquid or gas we may predict the behavior of any other, and therefore it seems eminently probable from equation (16) that since β has the same form for all substances, the form of the substance a for any simple liquid or gas will be found to be closely related to its form for any other simple liquid or gas.

Notwithstanding the indefiniteness given to equation (16) by our ignorance concerning the quantity a, in one respect the equation is explicit, and is again in direct antagonism to the equation of van der Waals. It follows directly from our equation that the pressure of any substance is greater than, equal to, or less than the corresponding pressure of a perfect gas, according as the attractive pressure is less than, equal to, or greater than zero. In other words, whenever the volume of any phase is greater than the volume that it would occupy as a perfect gas, a is negative, and the total resultant force between the molecules must be repulsive. Regarding such a repulsion, which finds no place in van der Waals' theory, it is true that there is little positive evidence, but what evidence there is seems to indicate decidedly the existence in some cases of some kind of a repulsive force. If a liquid is cooled at constant pressure, its

volume does not appear to tend to become zero at the zero of temperature, but rather to approach as a limit some definite volume. As the kinetic forces become less there must be some other force which enters to oppose the attraction between the molecules. If it is permissible to consider the limiting case where the motion of the molecules ceases, there must exist at the absolute zero a condition in which the total external pressure and all the attractive forces between the molecules are together balanced by some sort of outward force which is equal to their sum. This would be greater than the attractive forces alone, and the difference would depend upon the external pressure. In other words, there would be a resultant repulsive force equal to the external pressure. As to whether this force is of the nature of elasticity, or of some action at a distance, it would be presumptuous to speculate. From these considerations, which must be admitted to be very hypothetical, it would seem that at ordinary temperatures there should be analogous conditions in which the repulsive forces would be greater the higher the pressure. According to equation (16), in all liquids the resultant attractive pressure diminishes with increasing external pressure, and finally changes sign at the point where on the $P\,V$ diagram the equation of condition cuts the hyperbola of thermal pressure; that is, at the point where the volume is the same as it would be if the substance were to behave as a perfect gas under the same pressure. Similarly, at high pressures probably all gases have a greater volume than corresponds to the gas law, and according to our theory their particles repel each other under these conditions. At atmospheric pressure, on the other hand, almost all gases have too small a volume, but hydrogen still has a volume which corresponds in our theory to an intermolecular repulsion. It is interesting, therefore, to note that in the experiments of Joule and Thomson, while other gases showed an increase of internal energy on expansion, hydrogen showed a slight decrease. Helium is in all probability another gas which has too great a volume; and it has been shown by Donnan * from his experiments on the effusion of gases, that probably helium also has a heating effect on free expansion, like hydrogen. Such a heating effect can be explained in no other way so simply as by assuming that there is a repulsion between the molecules in both helium and hydrogen. Finally, a similar repulsion could explain the phenomenon observed in the experiments of Ramsay † on the distribution of hydrogen between two spaces, one of which contained hydrogen alone, the other hydrogen and nitrogen. He

* Phil. Mag., XLIX. 423 (1900).

† Phil. Mag., XXXVIII. 206 (1894).

found that, if the two spaces were connected by a semipermeable membrane, the partial pressure of the hydrogen was less in the space containing nitrogen. This could be easily explained by assuming a repulsion between a molecule of hydrogen and one of nitrogen, and this explanation is again in full accord with the observation of Joule and Thomson that hydrogen mixed with nitrogen greatly decreased the cooling effect of the latter when expanding through a porous plug. These bits of evidence, accumulated, point decidedly to the truth of equation (16).

It was stated above that in general a is a function of the temperature; for if either in equation (16) or in the equation of van der Waals the term representing intermolecular attraction should be independent of the temperature, it would follow immediately from thermodynamics that the specific heat at constant volume of a liquid or a vapor should be independent of its volume, and also that a liquid and its vapor should have the same specific heat at constant volume.* All our evidence, both experimental † and theoretical,‡ is opposed to this conclusion. There is little doubt that the specific heat at constant volume, even in gases, changes in all cases, and sometimes considerably, with an isothermal change in volume; and it may be noted that while the equation of van der Waals is incompatible with any deviation in the specific heat at constant volume, such a deviation is a direct consequence of our present theory. For, since the specific heat depends upon the energy required to raise a substance from one temperature to another, and since that energy, according to any kinetic theory, is partly consumed in increasing the kinetic energy of the molecules, the specific heat must depend in part upon the kinetic energy of the molecules at the two temperatures. According to the accepted kinetic theory the energy of progression of the molecules must be the same at any one temperature under all conditions. The energy required to increase the progressive energy of the molecules from one temperature to another would depend, therefore, on the two temperatures, and would be independent of all other circumstances. On the other hand, according to the views expressed on page 154, the kinetic energy of the molecules may vary at any temperature according to the other conditions of a substance. Let us consider a gas in which there is no attractive or repulsive force between the molecules. According to the theory hitherto accepted, if the volume occupied by the

* Cf. Nernst, Theor. Chem., p. 234 (1898).

† Joly, Phil. Trans. Roy. Soc., 182 A, 73; Proc. Roy. Soc., XLVII. 218; LV. 390.

‡ Lewis, These Proceedings, XXXV. 1 (1899); Zeit. Phys. Chem., XXXII. 364 (1900).

molecules * of the gas were appreciable, then the progressive energy of the molecules would be the same as if it were a perfect gas, but the pressure would be greater than the pressure of a perfect gas. According to our new theory the pressure in this case would be necessarily the same as that of a perfect gas, and therefore the kinetic energy of the molecules must be less than that of the molecules of a perfect gas. In general, then, we should expect the internal kinetic energy to diminish with the volume.

This is an important consequence of the new theory, and it is evident that the volume of the molecules must be as important in our theory as in that of van der Waals; but in the former the quantity "b" concerns energy relations, while in the latter it concerns pressure relations. We are thus led to a consideration of the total change in internal energy in an isothermal change of volume of a liquid or a gas, and in the change from a liquid to a vapor.

It has frequently been assumed that the energy change in such a process is a measure of the attractive forces which oppose or assist the process. In an earlier paper † I have shown that this is the case only when the specific heat at constant volume remains the same; and, in fact, it is obvious that the change in potential energy which is a measure of attraction is in general only one factor of the total change in energy which includes also any change in the internal energy of the molecules as well as the change in progressive energy of the molecules, which is assumed in our present theory.

These three factors will be designated as follows: The change in potential energy, or Free Energy, which is the measure of intermolecular attraction, will be represented by dX; change in the progressive motion of the molecules by dE; change in the internal energy of the molecules by dI. If dU is the total change in internal energy,

$$dU = dX + dE + dI. \tag{17}$$

In the paper ‡ already referred to I have developed the general thermodynamic equation of condition,

$$P = \frac{RT}{v} - F(v)\,T - \frac{dU}{dv} + T\int_{T_0}^{T}\frac{1}{T}\frac{dc_v}{dv}\,dT, \tag{18}$$

* This phrase is used in conformity to usage. The quantity "b" of van der Waals may be defined more generally and less hypothetically as a quantity depending on the difference between the time in which two molecules approach, collide, and separate, and the time which two mathematical particles would require for the same process.

† Lewis, l. c.

‡ Ibid.

where $F(v)$ is an unknown function of v, and c_v is the molecular heat at constant volume, T_0 some arbitrary temperature. Comparing this with equation (16), we obtain

$$a = F(v)\,T + \frac{d\,U}{d\,v} - T\int_{T_0}^{T} \frac{1}{T}\frac{d\,c_v}{d\,v}\,d\,T. \tag{19}$$

Now, substituting $d\,U$ from (17), and bearing in mind that $a = \dfrac{d\,X}{d\,v}$, we obtain

$$\frac{d\,E}{d\,v} + \frac{d\,I}{d\,v} = T\int_{T_0}^{T} \frac{1}{T}\,\frac{d\,c_v}{d\,v}\,d\,T - F(v)\,T. \tag{20}$$

This is the closest insight that we can obtain at present into the general form of $\dfrac{d\,E}{d\,v} + \dfrac{d\,I}{d\,v}$, but it is sufficient to show that in general the total change in energy is not identical with the change in potential energy, at least when $\dfrac{d\,c_v}{d\,v}$ is not zero.

If we could pass continuously from the liquid to the gaseous state, and equation (16) were assumed to hold good continuously throughout the process, the total work of the process could be found, and would be equal to the actual work done in the evaporation of the liquid. From equation (16),

$$\int p\,d\,v = \int \frac{R\,T}{v}\,d\,v - \int a\,d\,v,$$

or

$$\int_{v_1}^{v_2} p\,d\,v = R\,T \ln\frac{v_1}{v_2} - \int_{v_1}^{v_2} a\,d\,v;$$

or, since $a = \dfrac{d\,X}{d\,v}$, the total work is

$$R\,T \ln\frac{v_1}{v_2} - \int_{v_1}^{v_2} d\,X.$$

The work done in evaporation at the same temperature is $P'(v_1 - v_2)$, where P' is the vapor pressure. We may write, therefore,

$$P'(v_1 - v_2) = R\,T \ln\frac{v_1}{v_2} - \int_{v_1}^{v_2} d\,X.$$

Now, if $d\,X$ were always equal to $d\,U$, we could write

$$R\,T \ln\frac{v_1}{v_2} = (U_1 - U_2) + P'(v_1 - v_2) = L, \tag{21}$$

where L is the common heat of evaporation.

Now, as a matter of fact, $R\,T \ln \frac{v_1}{v_2}$ is always less than L, and this is precisely what would be predicted from our theory; for in passing from a liquid to a vapor energy must be used not only in overcoming the intermolecular attraction $\left(\text{the quantity that would be equal to } R\,T \ln \frac{v_1}{v_2}\right)$, but also in providing for the increase in the progressive energy of the molecules, which was shown on page 165 to be a necessary consequence of our theory.

In concluding this brief treatment of some of the consequences of our theory, we may mention one that is important in the study of homogeneous equilibrium. The isothermal, according to our present view, is not identical with the line of constant internal energy of progression of the molecules, which might also be called the line of constant molecular velocity; the latter line must, therefore, be of considerable independent importance; for if we regard the mass law kinetically as an expression of the law of probability, the chance of any two molecules reacting must depend upon their momentum at impact, and this would be constant along the line of constant molecular velocity, and not along the isothermal. The mass law, then, disregarding other disturbing factors, should hold along the former line rather than the latter. On account of an entire lack of data that would give any experimental evidence on this point, this mere suggestion of a possible future modification in the theory of chemical kinetics must suffice.

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INTERNATIONAL ATOMIC WEIGHTS.

By Theodore William Richards.

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Near the close of the year 1897, the German Chemical Society appointed a committee to select values of the atomic weights for common use in Germany. The confusion arising from the use of different values, and especially of different standards of reference, had become unbearable. After nearly a year's deliberation, they announced their conclusion that it is expedient to call oxygen exactly 16, and to refer other elements to this standard. They published a carefully considered and conservative table of values,* which immediately gained wide acceptance, partly because of its intrinsic merits, and partly because it was vouched for by such eminent men as Landolt, Ostwald, and Seubert. At the close of the remarks accompanying this table, the three members of the committee expressed their hope that the matter might be clinched by international agreement. The hope was strengthened by the fact that the two other modern tables, those of Clarke and of Richards, differed but slightly from the table presented in Germany. Time has strengthened this hope still further, for the two subsequent yearly editions of the three tables have steadily tended toward the elimination of earlier differences, until now they are even more alike than they were at first. †

On March 30, 1899, having been encouraged by the favorable reception of their work, the German committee issued to all important associations interested in chemistry throughout the world a general invitation to appoint delegates to an International Committee. ‡ The number of delegates was not determined, and the outcome was the appointment of fifty-seven men from among the most eminent chemists of eleven nations. As representatives on this International Committee the American Chem-

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* Ber. d. deutsch. chem. Gesell., **31**, 3761 (1898).

† See Journ. Am. Chem. Soc., **22**, 78 (1900); also, These Proceedings, **35**, 621 (1900), and Ber. d. deutsch. chem. Gesell., **33**, 1 (1900).

‡ Ber. d. deutsch. chem. Gesell., **31**, 2949 (1898); **33**, 1847 (1900).

ical Society appointed Professors F. W. Clarke, J. W. Mallet, E. W. Morley, T. W. Richards, and E. F. Smith. Shortly afterward the American Academy of Arts and Sciences added Professors Wolcott Gibbs and Ira Remsen to the list of American delegates. Besides these seven men, the present International Committee contains fifteen from Germany, eleven from Austria, eight from England, five from Belgium, three each from Switzerland and Italy, two from Japan, and one each from Holland, Russia, and Sweden. It is much to be regretted that Denmark, France, and Norway have as yet made no appointments.

Having thus received very general support, the German committee, in October, 1899, decided upon another step. They forwarded to each member of the International Committee a circular letter containing three questions, which were speedily answered by nearly all of the delegates. A literal translation of these questions follows: —

"1. Shall $O = 16$ be fixed as the future standard for the calculation of atomic weights?

"2. Shall the atomic weights be given with so many decimals that the last figure is certain within half a unit, or what other procedure shall be adopted?

"3. Is it desirable that a smaller committee should be formed, which should undertake the continual revision of the yearly atomic weight table and its publication? In case of agreement upon this point, it is proposed that each association name a single delegate to this smaller committee."

The forty-nine answers to these questions are highly interesting.* As regards the first question, only seven chemists (one American and six Germans) were decidedly in favor of retaining hydrogen as the standard, while forty were decidedly of the opposite opinion. Two were willing to accept either or both standards of reference. In spite of the fact that men as eminent as Professors Mallet, Volhard, Winkler, and Wislicenus are in the minority, the majority is so overwhelming that we must look upon this point as settled for a long time. Even if the probable delegates from the unrepresented countries should all vote in the negative, the majority must remain in favor of $O = 16$. Thus the new term, "international atomic weight," is perfectly clear and unequivocal in its meaning as to the standard of reference, and an important step has been made.

It may not be irrelevant here to enumerate the advantages and disad-

* Ber. d. deutsch. chem. Gesell., 33, Heft 12, p. 1850 (1900). The answers are published in full.

vantages of this international standard. In the first place, it is evident that the question is a practical one, not a theoretical one. If Prout's ancient hypothesis seemed at all probable, there would indeed be a strong reason for assuming hydrogen as unity; but Prout's hypothesis cannot now claim serious consideration, at any rate in its original form. No other theoretical reason for calling hydrogen exactly 1.000 is known to me. What, then, are the relative *practical* advantages to be gained by taking hydrogen or oxygen as the standard? In the first place, the precise quantitative analysis of compounds containing hydrogen is a very difficult matter, and water is the only one which has been adequately studied. Hence nearly all atomic weights must be referred to hydrogen through the medium of oxygen; and if the ratio H : O is found to be even a little in error, all other values must be recalculated. Morley's work on this ratio is indeed magnificent, and it is not likely that his accuracy can be surpassed for a long time; nevertheless the principle still remains. Oxygen, on the other hand, has been directly compared with many metals, as well as with potassic chloride and similar salts obtainable from the chlorates and their analogues. Hence from the point of view of directness of comparison, oxygen is to be preferred. Silver might be even better, as Erdmann and Volhard point out in their replies to the circular letter; but the question does not concern the starting of an entirely new system, but rather the choice between two old ones.

Another point to be considered is the effect of the decision upon the data contained in the past literature of chemistry. Any change which might confuse the understanding of the work of the past would be indeed a grievous one; and a change to O = 15.879 could not but have this effect. Little or nothing has been written with the assumption of this standard, while a great bulk has been written with the assumption O = 16. The confusion caused by the inaccurate value O = 15.96 is quite bad enough, without the introduction of a new stumbling-block. Moreover, in the gas constant and a multitude of other physico-chemical constants the value O = 16 enters, and a change in this standard would complicate the use of a great mass of valuable literature of this kind.

Another, although somewhat trivial, reason why oxygen should be taken as 16 is because in that case a somewhat larger proportion of the atomic weights approximate whole numbers than would be the case otherwise.

The chief objection to the proposed standard is a pedagogical one. It is claimed that confusion is caused in the mind of the elementary student

by the use of the number 1.0075.* The German committee points out in its last report that this difficulty may be avoided by giving the elementary student only the round numbers (which suffice amply for his purpose), accompanied by the statement that these are rough approximations. There is obviously another way of avoiding the confusion, and that is by doing away with hydrogen as a standard of specific gravity. The difficulty of preparing this gas in a pure state and its great lightness are arguments against it, in any case. Moreover, in my experience the simplicity of the relationship between the specific gravity referred to hydrogen and the molecular weight is quite as likely to be a stumbling-block as an assistance. Many a beginner learns by heart the statement that the specific gravity is twice the molecular weight; for he does not pause to think about it and see that he has inverted the ratio. If, on the other hand, the specific gravity of oxygen is taken as the standard, the adverse arguments disappear, and even a dull student can hardly forget the reason why the specific gravity of the gas X referred to oxygen must be multiplied by 32 to give the molecular weight. For several years I have used this method with large classes, and find that it gives no trouble. The only data needing recalculation are the specific gravities of the gases, and that is a simple matter. It seems to me, by the way, that the use of 2 instead of R in physico-chemical formulae has the same pedagogic fault of obscuring the source and nature of the symbol.

The answers to the second international question, which seeks to determine the number of decimal places to be given, support the German committee in its position with a majority almost as overwhelming as in the case of the first question. The minority of eight consists of three Americans, three Germans, and two Japanese, all the others desiring to omit all figures which are not certain to within half a unit. The committee, in summing up the opinions upon this subject, states that its desire is to propose a table for common use, and that the minority, which desires the retention of one uncertain decimal place, has rather had in mind the requirements of work of the greatest precision. Undoubtedly the curtailed table will answer for most purposes, but it seems to me that the nature of the decimal notation causes an unfortunate incompleteness in it. Although, in the face of so great a majority, this matter, like the other, must be considered as settled, I am tempted to call attention to this incompleteness in relation to numerical data of all kinds.

* Much has been written upon both sides of this question. Besides the articles already referred to, many references may be found in two papers by Küster and Brauner (Zeit. anorg. Chem. **14**, 251 and 257 respectively (1897)).

Let us consider a concrete example, — the case of nitrogen. Few would be willing to contend that the last figure in the number 14.04 is certain. For the sake of argument, let us assume that the value of this atomic weight may really be as low as 14.034 or as high as 14.046. According, then, to the rule which has just been adopted by the International Committee, this figure 4 should be omitted, and nitrogen should be called 14.0. Such an omission causes an error far greater than the uncertainty which leads to the dropping of the figure. The uncertainty named above is only 0.04 per cent, but the minimum error in the value 14.0 is 0.24 per cent, if the lower value given above is supposed to be the lowest possible. Clearly one must either record uncertain figures, or else omit figures which have a real significance. The dropping of a decimal place at once reduces tenfold the ability of a number to express slight changes of value; but numerical results may have any degree of accuracy, and cannot be classed strictly into classes separated by gaps so wide. For this reason it is a well-known practice in scientific calculation to retain during the calculation one uncertain figure, while a final result is sometimes relieved of this uncertain figure. According to this rule, the table of atomic weights should always give an uncertain figure in each value; for atomic weights are simply data for further calculation. If this is done, the user has all the truth, and may reject as much of it as his occasion permits. Such a table of atomic weights seems to me to be the best, because it is capable of fulfilling all uses.

Quite another point of view should be adopted in making a table solely for common use. Here we are concerned not with the number of certainly ascertained figures which may have been determined by Stas, but rather with those figures which will have an influence upon the work in hand. Usually the error in such a value is important not on account of its absolute magnitude, but rather on account of its relation to the value itself. In short, the percentage error is that which ought to be considered in constructing a table of atomic weights for common use. A majority of chemists would probably decide that a table in which the values were within 0.1 per cent of their true values would serve all ordinary purposes. Most common methods are not able to attain as great a degree of accuracy even as this, but the admission of a wider range of inaccuracy in a table of atomic weights might by summation cause an appreciable error. Silver might be called 108.0, chlorine 35.5, bromine 80.0, iodine 126.9, potassium 39.2, sulphur 32.1, and lead 207.0, without seriously affecting the results of most quantitative work, and indeed every one frequently uses such approximate values. Even in this approximate

table hydrogen should be 1.008, and not 1.01, if the percentage rule is to be followed.

The last question asked by the German committee, suggesting the appointment of a small standing committee, was answered affirmatively by every one. The original plan of having a representative from each society would evidently result in the formation of an unwieldy body; hence the German committee has wisely concluded that a small number, perhaps three, one each from Germany, England, and the United States, should be elected from among those who have had especial experience in the matter of atomic weights.

The matter is by no means finished. The German committee asks any one who has anything new to say upon the questions under consideration to send a brief statement of his views to Professor Landolt before November 15; and some new ideas may have been advanced in the discussion in Paris at the end of July. The balloting for the election of the smaller International Committee is already in progress.

The German Chemical Society, as well as the members of its committee, is greatly to be congratulated on the success of the undertaking, not only because of the immediate gain to chemistry, but also because of the manifest advantages of the growth of scientific coöperation between men of all nations.

MT. DESERT, MAINE, August 6, 1900.

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CONTRIBUTIONS FROM THE ZOÖLOGICAL LABORATORY OF THE MUSEUM OF COMPARATIVE ZOÖLOGY AT HARVARD COLLEGE, UNDER THE DIRECTION OF E. L. MARK. — No. 118.

PERIPHERAL DISTRIBUTION OF THE CRANIAL NERVES OF SPELERPES BILINEATUS.

By Mary A. Bowers.

With Two Plates.

CONTRIBUTIONS FROM THE ZOÖLOGICAL LABORATORY OF THE MUSEUM OF COMPARATIVE ZOÖLOGY AT HARVARD COLLEGE, UNDER THE DIRECTION OF E. L. MARK. — No. 113.

No. 11. — PERIPHERAL DISTRIBUTION OF THE CRANIAL NERVES OF SPELERPES BILINEATUS.

By Mary A. Bowers.

Presented by E. L. Mark, June 14, 1899. Received August 20, 1900.

Contents.

A. Introduction.

The study of the distribution of the cranial nerves of Spelerpes bilineatus was undertaken merely as introductory to an intended investigation of the central origin of the nerves; but it has seemed advisable to make this study more careful and detailed than was at first contemplated, and as a result the nerve roots have as yet been but superficially examined.

By studying the "components" of the individual nerves, following in

some degree the method adopted by Strong ('95), it has seemed possible to make out more accurately the homologies of Urodelan and Anuran nerves than has before been done.

The color scheme used by Strong has been followed as closely as practicable; roots and ganglia, however, have been left neutral from lack of knowledge of the exact proportions of the different components passing through the ganglia. Strong's nomenclature has also been adopted, since it proves quite as applicable to the Urodelan as to the Anuran type. The confusion which would have arisen from the use of two or more sets of terms is thus avoided.

My work has been carried on in the Radcliffe College Laboratory at the Museum of Comparative Zoölogy, Cambridge; and it is with great pleasure that I acknowledge here my indebtedness to the Director of the Laboratory, Professor E. L. Mark, who has assisted and advised me, and helped me in many ways. I also wish to express my sincere thanks to Dr. Harris H. Wilder and Dr. B. F. Kingsbury, who have kindly preserved and sent to me all my Spelerpes material.

B. Methods.

Several methods of preservation and staining were tried, but the material preserved in four per cent formalin and stained with Heidenhain's iron haematoxylin was the most satisfactory. The decolorizing process was stopped at the moment when the other tissues had given up their stain but the nerves still retained the deep blue color imparted to them by the haematoxylin. It was in this way that the series which served for the reconstructions were made. The sections were cut parallel to the sagittal plane through the left half of the head of a larva 23 mm. long, and were 20 μ thick. Figures 1 and 3, representing the nerves of the left side as projected on the sagittal plane, were made by outlining the accurately superposed images of the successive sections given by an Abbé camera. To insure the proper superposition, direction planes were employed. Before sectioning, the paraffine block was cut in prismatic form, the bounding planes being perpendicular to the prospective plane of sectioning; the faces of the prism were painted with a mixture of lamp-black and turpentine; the block was then quickly immersed in rather soft paraffine and again trimmed before sectioning. The rim of black around each section afforded a satisfactory means of accurate superposition.

Figures 2 and 4, representing projections on the frontal plane, were constructed from the same series, by plotting on millimetre paper the positions of the nerves as they occurred in the successive sections.

C. Eye-muscle Nerves, III., IV., and VI. (Pl. 2, Figs. 3, 4).

It was my intention to confine my work to the fifth, seventh, ninth, and tenth nerves, but in my examination of the ophthalmic branch of the trigeminus it became necessary to make a study of the eye-muscle nerves, from which some facts of interest were established. I therefore give a brief account of these nerves, — the third, fourth, and sixth cranial nerves.

The *oculomotor* (III.) arises, as usual, from the floor of the mesencephalon, passes through the brain wall, and then, lying between that wall and r. ophthalmicus V. (*V. opt.*), immediately gives off its r. superior (Pl. 2, Figs. 3, 4, III. *rt. su.*) to m. rectus superior. It then passes under r. ophthalmicus V., — which takes a more median position (Fig. 4), — and here lies for a short distance in close contact with a branch of the abducens (VI.) In some series of sections the two nerves, while indistinguishable on one side of the head, were clearly separable on the other. There is, then, no real fusion of the two.

A cluster of ganglion cells (*cl. gn.*) is constantly found enveloping that portion of the oculomotorius that lies directly ventrad to the optic nerve (see Figs. 3, 4). In the 23 mm. stage these ganglionic cells are grouped into a compact mass, but in older stages (40 mm.) they are somewhat scattered along the nerve. The oculomotorius follows closely m. inferior rectus, giving fibres to it, and ends in m. inferior obliquus.

The *trochlearis* (IV., Pl. 2, Figs. 3, 4) is very minute, and its whole course was not traceable in the 23 mm. stage; but in older larvae an interesting condition was observed. At the posterior margin of the eyeball this nerve joins a dorsal branch of r. ophthalmicus (*Va*), and the two run along the median dorsal surface of the eyeball to near its anterior margin as one nerve. Here the fibres of the trochlearis (*IV. ob. su.*) pass ventrad and are distributed to the superior oblique muscle; this ophthalmic branch of the fifth (*Va*) then passes forward and dorsad to innervate the skin in the regions in front of the eye. Since IV. joins the dorsal branch of V. on its dorsal side and separates from it on the ventral side (Fig. 3), there must be a crossing of fibres; this crossing I found clearly shown in sagittal sections of one of my older embryos. Gaupp ('97, p. 136) speaks of this relation of IV. and V. in the frog, and presumes that the branch given off to m. superior obliquus is composed of fibres from IV., but he did not actually observe the crossing of fibres.

For the study of the *abducens* (VI.), Spelerpes proved to be especially advantageous. In this species the abducens does not enter the Gas-

serian ganglion, as it does in some of the Amphibia, but (Fig. 3) comes into contact with the ventral side of r. ophthalmicus V. (*V. opt.*) a short distance anterior to its emergence from the ganglion. Owing to this condition it is much easier to follow the fibres of the two nerves in this species than in those where the two nerves emerge from the ganglion together. Herrick ('94, p. 200) describes for Amblystoma two branches of the sixth nerve, one of which goes to m. rectus externus, the other to m. retractor bulbi, but he thinks the branch to the latter muscle ought really to be assigned to the trigeminus, and so colors it in his figures. Although in Spelerpes the sixth lies in immediate contact with r. ophthalmicus V., yet I was able to trace its fibres with accuracy in several series of preparations, and am certain that there is no ventral branch given off from V., but that VI. divides into two branches, one (*VI. rt. ex.*) going to m. rectus externus, the other (*VI. ret. bl.*) to m. retractor bulbi. On the latter branch was found, in the region indicated by *cl. gn'*. (Pl. 2, Figs. 3, 4), a distinct aggregation of ganglionic cells, similar to those enveloping the oculomotorius. I have found no reference to such cells connected with the sixth nerve, except in one sentence of Strong's article ('95, p. 134), where he says: "There seem to be ganglion cells in connection with it [abducens] (703), although these may belong to the oculomotor nerve." I have not yet tried methods to show the connection of these ganglionic cells with the nerve fibres. Only two roots were found, as in Necturus; these emerge from the ventral side of the medulla in about the same transverse plane as the most anterior roots of IX. + X.

D. Trigeminus.

(1) *Roots.* — The little study which I have hitherto given to the roots of the cranial nerves in Spelerpes has shown that there is apparently a close correspondence to the condition found by Kingsbury ('95.) in Necturus.

Fibres forming the trigeminus root are: (1) a large ascending bundle (Plate 1, Fig. 2, *V. rx.*) of mostly small fibres lying ventrad to the eighth nerve, presumably the ascending tract of the fifth, though they were not traced back into the dorsal column of the spinal cord. It is possible that fibres from a sensory nidus (terminal) may be associated with these, as in Necturus; but none were distinguished; (2) two small, presumably motor, bundles of large, deeply staining fibres (*V. rx. mot.*), which arise from the floor of the metencephalon and join the ventral side of the ascending tract of the fifth, just before its exit from the brain;

(3) coarse fibres from the roof of the mesencephalon (not shown in the Figures), which curve ventrad and caudad and pass out of the brain with the other roots of the fifth. After emergence from the brain, the trigeminal fibres run obliquely cephalad and laterad, as indicated in Figures 1 and 2 (Pl. 1), and can be traced through the ventral half of the Gasserian ganglion into rami ophthalmicus, maxillaris, and mandibularis. The fibres are of medium size and in iron haematoxylin take a *grayish* blue stain, in sharp contrast to the large fibres from the seventh nerve, which take a *deep* blue stain. The latter run through the dorsal part of the ganglion, from which they emerge as r. ophthalmicus superficialis VII. and r. buccalis VII.

(2) *Branches.* — (*a*) *Ramus ophthalmicus trigemini* (Figs. 1–4, *V. opt.*) leaves the anterior mesial part of the Gasserian ganglion, runs directly cephalad, and comes in contact with III. and VI., as already (pp. 181 and 182) described. Just posterior to the eye, in the transverse plane in which the optic nerve emerges from the cartilage of the brain wall, the ophthalmicus trigemini gives off a large dorsal branch (*Va*, Figs. 1, 3, 4). From this branch arise two small branches Va^1 and Va^2 (Fig. 3). The more posterior and lateral of the two branches (Va^1) follows m. rectus superior to its insertion on the eyeball.

The other branch (Va^2) goes to the skin of the dorsum ; it divides, sending one branch cephalad and another caudad. The main branch (*Va*) curves along the dorsal median surface of the eye (Figs. 1, 3, 4) in connection with IV. (Fig. 4), as previously described, and is distributed to the skin in the region in front of the eye.

Ramus opthalmicus V., after giving off the dorsal branch (*Va*) just described, takes its usual course forward, above the optic nerve (Fig. 3), close beside m. rectus internus, and divides into three branches (Figs. 1–3). The most ventral of these (*V. l. na.*) curves around in front of the eye to the skin of the external nares and cheek ; it corresponds to Gaupp's r. lateralis narium. The middle one of the three branches curves ventrad and anastomoses (*coms.*) with r. palatinus VII. This condition agrees with that found by Herrick in Amblystoma. Strong ('95, p. 122) also finds an anastomosis of these two branches in the tadpole, but it takes place farther cephalad than in Spelerpes. The anastomosing nerves continue cephalad after their union, but could be traced only a short distance in the loose tissue in the roof of the oral cavity, just median to the internal nares. The most dorsal of the three branches (*V. m. na.*) of the ophthalmicus (Gaupp's r. medialis narium) runs above the olfactory and innervates the skin at the tip of the nose.

(*b*) *Ramus maxillaris trigemini* emerges from the Gasserian ganglion in the same transverse plane with r. buccalis and r. ophthalmicus superficialis VII., and the three appear (Fig. 2) as one nerve for a short distance, as they pass laterad and cephalad between m. temporalis and m. masseter. While ramus ophthalmicus superficialis VII. separates from the others and curves mesiad, rami maxillaris V. and buccalis VII. pass cephalad along the dorso-lateral surface of the masseter muscle. In many of the specimens examined the two appear like one nerve, but the difference in the size and distribution of the fibres was always noticeable, and in the series of sagittal sections used for reconstructions they were clearly separate. R. maxillaris (*V. mx.*) gives off a small general cutaneous branch, not shown in the drawings, to the dorsum immediately after leaving the ganglion, and its final distribution is to the skin of the cheek. It does not anastomose with ramus palatinus VII., as is the case in the tadpole of Rana (Strong).

(*c*) *Ramus mandibularis trigemini* (*V. md.*) leaves the ganglion directly below ramus maxillaris, passes ventro-laterad, gives off first a branch ($V\beta$) to m. masseter, next, two more small branches (not figured) to the same muscle, and then a fourth ($V\gamma$), which runs dorsad to m. temporalis. In the same transverse plane with $V\gamma$ there arises a cutaneous branch ($V\delta$), which runs ventro-laterad and is distributed to the skin posterior to the angle of the jaw. It comes into very close connection with the more anterior branch of ramus mandibularis externus VII.; in some series of sections it even appears to anastomose with this branch of VII.; but other sections show conclusively that it does not. Another general cutaneous branch ($V\epsilon$) is given off from ramus mandibularis V. to the angle of the jaw, a small twig from it turning caudad; the main branch ($V\epsilon$), however, runs forward, close above ramus mandibularis externus VII. to the skin of the lower lip. A division of the main nerve into nearly equal parts (*V. md. i.* and *V. md. ex.*) soon occurs. A musculo-cutaneous branch (*V. md. i.*), Gaupp's ramus mandibularis internus V., passes ventrad between os dentale and Meckel's cartilage to the lower side of the jaw, where it innervates m. mylohyoideus and the skin superficial to it. The other branch (*V. md. ex.*), which is purely cutaneous, remains on the upper side of the jaw and is distributed to the skin of the lower lip. It corresponds to Gaupp's ramus mandibularis externus V.

E. Facialis and Acusticus.

1. *Roots.* — Apparently the roots of the facial and acoustic nerves (Pl. 1, Figs. 1, 2) agree with the condition in Necturus as described by Kingsbury ('95); at least the relation of the several components as they emerge from the brain is the same. Most caudal and ventral is the motor root of the facial (*VII. rx. mot.*),* formed from two rootlets of deeply staining fibres, which arise from the median ventral region of the medulla. Dorsal to this emerges the one large root of the acoustic (*VIII. rx.*), and close to the dorsal side of the latter the fine unstained fibres of the fasciculus-communis root of the facial (*VII. rx. fas. com.*). At a little distance dorsad to these three roots and a little more cephalad emerge the very coarse, deeply staining fibres of the lateral-line root of the facial (*VII. rx. ln. l.*).† This is the "dorsal VII." of Strong. The fibres of this root are not grouped into two distinct rootlets, as in Necturus, though from the appearance of some sections there seems to be a tendency toward such a grouping. Immediately on leaving the brain the fibres of this component unite with those of the three roots ventral to it, forming a continuous dorso-ventral sheet (Fig. 1).

The dorsal root (*VII. rx. ln. l.*), however, quickly divides, and its more ventral fibres curve ventrad and laterad to enter the acustico-facialis ganglion (*gn. ac.-fac.*), while its more dorsal fibres pass directly cephalad along the mesial surface of the ear capsule in the form of a thin dorso-ventrally expanded sheet (compare Fig. 2), and enter the Gasserian ganglion.

This dorsal part of the lateral-line root of VII. contains ganglionic cells, which lie dorsal to those of the Gasserian ganglion proper, with which, however, they become fused into a common mass. Nevertheless, the fibres of this portion of the lateral-line root are clearly traceable in their passage through the Gasserian ganglion, from which they emerge as two.

2. *Branches.* — (*a*) *R. ophthalmicus superficialis* (*VII. opt. suf.*) *and* (*b*) *r. buccalis* (*VII. buc.*) *of the seventh nerve.* Both of these branches are distributed to lateral-line organs, the former giving off numerous twigs throughout the whole of its course from the ganglion to the tip of the nose. Ramus buccalis VII. has already been referred to as following closely the course of r. maxillaris V. (see Fig. 2), though

* By an oversight this is lettered in Fig. 1 as *VI. rx. mot.*

† Not lettered in Fig. 1. In this figure it is almost directly below the lettering "*rm. aur.*"

it extends farther anterior than the latter. (*c*) *The acusticus.* Three of the branches of the eighth nerve have been represented in the drawings in neutral tint, — ramulus ampullae anterioris (*rml. amp. a.*), ramulus ampullae externae (*rml. amp. ex.*), and ramulus ampullae posterioris (*rml. amp. p.*). These were plotted simply to show their relation to the seventh nerve. Fibres to the macula ac. sacculi and macula ac. neglecta were observed, but these were only slightly differentiated at the stage here reproduced. They could be clearly traced in a larva 40 mm. long. The anterior portions of VII. and VIII. remain connected with each other until after r. palatinus VII. is given off; the acoustic then curves dorsad and enters the ear capsule, while the facialis curving ventrad and ectad passes out through the cartilage of the skull.

The first of the branches to be given off from the ventral part of the facialis is the (*d*) *r. palatinus*, whose fibres are derived exclusively from the fasciculus-communis component. The ganglion of this root, lying close to the point where r. palatinus emerges, is fused with that of the eighth nerve and "represents probably the geniculate ganglion" (Kingsbury, **'95**, p. 187). The fibres of this component are always easily recognizable, since they are very fine and with iron haematoxylin take only a faint stain, or sometimes none at all. The greater portion of the fibres of the fasciculus communis goes to form this branch (r. palatinus), which passes directly cephalad, giving a few fine branches to the roof of the pharynx, and anastomosing, as already stated, with r. ophthalmicus V.

The few remaining fibres of the fasciculus communis pass out through the ventral wall of the ear capsule with the hyomandibular portion of the facialis, run through the ganglion of the lateral-line component of the facialis, which lies beneath the cephalic end of the otic capsule, and emerge as (*e*) *r. mandibularis internus VII.* (*VII. md. i.*), or *r. alveolaris VII.*, which Strong (**'95**, p. 187) homologizes with the chorda tympani of higher vertebrates. In Spelerpes this branch is very minute, and in the sagittal sections used for reconstruction could be traced only a short distance anterior to the articulation of the jaw (Figs. 1, 2); but in transverse sections it could be traced along the inside of the jaw to its termination in the ventro-lateral wall of the pharynx. It does not, in any part of its course, enter a canal, agreeing in this respect with Siren lacertina as described by Wilder (**'91**).

(*f.*) *R. mandibularis externus VII.* (*VII. md. ex.*), or *r. mentalis VII.*, the ventral part of the lateral-line component of the seventh, passes ventrad and cephalad from its ganglion, which lies under the otic capsule,

and soon divides into two nearly equal branches, both of which first run ventrad into the lower jaw, then cephalad, nearly parallel to each other, to the tip of the chin, supplying the lateral-line organs along their course. One of these (*VII. md. ex.'*) is more ventral and median than the other (*VII. md. ex.*). Strong ('95, p. 134) says of this branch in Amblystoma: "It is a cutaneous nerve; and probably, as in the tadpole, supplies the lateral sense organs." Its ganglion is "composed of large ganglion cells." Herrick ('94, p. 199), however, found no ganglion in the course of the r. mandibularis externus in Amblystoma.

Strong ('95, p. 163) has called attention to the fact that the r. buccalis of von Plessen und Rabinovicz is misnamed, that it corresponds to r. mandibularis externus VII., and is derived from the ventral division of the lateral [*i. e.* lateral-line] root. Apparently a further interpretation of their designations must be made, for their "Begleiter des R. hyoideo-mandibularis" (their ramus hyoideo-mandibularis and by inference its "Begleiter" are distributed to the skin of the cheek and the lower jaw) also clearly belongs to the lateral-line component. It is probable that, while their r. buccalis corresponds to one of the two branches (the more lateral, *VII. md. ex.*) of r. mandibularis externus VII. as found in Spelerpes, their "Begleiter" corresponds to the other (the more nearly median, *VII. md. ex.'*) branch.

Herrick ('94, p. 199), following too closely von Plessen und Rabinovicz, has repeated for Amblystoma their mistake concerning this "Begleiter." He describes the ramus buccalis and the accessory ramus hyomandibularis ("Begleiter") as following the ectal aspect of the jaw bone to the tip of the lower jaw, and as being distributed to the skin. He says: "The fibres of the ramus buccalis are mainly, if not wholly, derived from the dorsal root, as Strong has pointed out. The nerve which I have called the accessory hyomandibular seems to be the same as Strong's 'small branch to lower jaw,' which he derives from the fasciculus communis and considers the representative of the chorda tympani of higher forms." But obviously the homologue of Strong's "small branch to lower jaw" is not Herrick's accessory hyomandibular, but his r. alveolaris.

(*g.*) *R. hyomandibularis VII.* in Spelerpes is very short, as compared with its length in the tadpole. In the latter, it is prolonged, as it were, almost to the anterior margin of the eye before its first branch, r. hyoideus VII., is given off. The condition in Spelerpes corresponds more nearly to that in the adult frog. Presumably the 23 mm. larva of Spelerpes undergoes much less alteration in the course of its further development than does the tadpole, so that the two stages are not

directly comparable. Evidently the name r. hyomandibularis must be restricted in Spelerpes to the short trunk of the ventral part of the seventh, which is included between the region of its separation from the eighth and that of the giving off of r. hyoideus. Though much shorter than in the tadpole, it is made up of the same components, except that it does not embrace the general cutaneous. This constituent is represented exclusively by the communicating branch from IX. to VII. Since in Spelerpes this r. communicans IX. ad VII. is not received by the hyomandibular trunk of seven, but by r. hyoideus after its separation from the trunk (Fig. 2), it is probable* that no general cutaneous fibres are included in the hyomandibularis proper. This, however, is not a fundamental difference, being merely a question of the earlier or later accession of r. communicans to branches of the seventh. In one point, only, is a greater importance to be noted: r. mandibularis ext. in Spelerpes probably does not contain, as in the tadpole, a general cutaneous component.

The (*h*) *r. hyoideus* after receiving r. communicans from IX.+X, curves latero-ventrad and is distributed to m. digastricus and m. mylohyoideus posterior and to the skin ventral to them. The main branch (VII. *hoi.*) is figured in neutral tint, since the proportion of the two components was not accurately ascertained.

F. Glossopharyngeus and Vagus.

1. *Roots.* — The roots of this group, like those of the seventh and eighth, show apparently a close correspondence to the condition in Necturus, though a careful comparison will be necessary to determine this with certainty. The most cephalic and most dorsal root is the lateral-line component (Pl. 1, Figs. 1, 2, $IX.^{1+2}$); it resembles dorsal VII. in appearance and position. In this case, however, the root is composed of two bundles. It is equivalent to Kingsbury's $IX.^{1+2}$ and to Strong's first root of IX.+X.

The second root ($IX.^{3+4}$) emerges one section (20 μ thick) caudad and slightly ventrad of the first root; it is composed of (1) the characteristic fine colorless fibres of the fasciculus-communis component and (2) a ventral bundle, presumably motor. It corresponds to Kingsbury's $IX.^{3+4}$ and to Strong's second root.

The third root ($X.^1$), the equivalent of Kingsbury's $X.^1$, emerges

* It is of course *possible* (?) that some fibres from the r. communicans take a centripetal course in the r. hyoideus and thus reach the hyomandibular trunk of VII.

at some distance caudad of the preceding and is made up of three components: (1) most dorsal, fine fasciculus-communis fibres, (2) more ventral and caudad of fasc. com. a large bundle of coarser fibres (ascending X.), which correspond to those of ascending V., and (3), in this differing from Necturus, a ventral bundle (motor ?). The third root in the tadpole has, according to Strong, the same triple composition, but in that animal the fasciculus-communis fibres emerge ventral to those of ascending V., not cephalad of them, as in Spelerpes.

The remaining four roots are small and could not be traced in the sagittal series of the 23 mm. larva; but they were plotted on the frontal reconstruction (Fig. 2) from frontal sections of another 23 mm. specimen, and the results were checked by the study of other series of (transverse) sections. These four roots all appear to be motor, for they arise in the same horizontal plane from ventral fibres, which turn cephalad after emerging from the medulla. Kingsbury's $X.^2$, $X.^3$, and $X.^5$ are in his opinion motor, but he says that $X.^4$ is probably sensory, and that its fibres accompany those of ascending V.

2. *Branches.* — The *coarse* fibres of the first root in Spelerpes can be easily traced through the upper part of the ganglion IX.+X., and all but a few of them, which are given off dorsally (see Fig. 1, *rm. su'tp.*), pass out at the posterior end of the ganglion as the lateral-line nerves — (*a*) *ramus lateralis* — to be distributed to the lateral-line sense organs of the body.

The remaining coarse fibres form a branch (*rm. su'tp.*) which passes dorsad and ectad and divides into two small branches which innervate sense organs just posterior to the ear. Following Strong's nomenclature, this may be called (*b*) *ramus supratemporalis*, though it does not curve cephalad, as in the tadpole. It may be noted in passing that the "ectad tendency" of the cranial nerves in Spelerpes, as compared with the "cephalad tendency" in the tadpole, is a noticeable difference between the two forms, and is probably due to the more anterior position of the gills in the tadpole.

There is a bundle of general cutaneous fibres (*rm. aur.*), which leaves ganglion IX.+X. in company with r. supratemporalis, from which, however, it immediately separates and runs dorso-cephalad to the skin above the ear capsule. It corresponds in composition and distribution to the branch called by Strong (*c*) *ramus auricularis*, and known in the frog as r. cutaneus dorsalis.

From the cephalo-lateral portion of the ganglion there pass out three branches, which for a short distance are united into a single trunk. The

first branch to separate from the trunk is (*d*) *ramus communicans ad facialem* (*rm. comn.* IX.–VII.), which follows the latero-ventral surface of the ear capsule till it unites with r. hyoideus VII., as already described. Strong ('95, p. 130) gives reasons for considering this branch a general cutaneous; its relation to VII. in Spelerpes would seem to add evidence of the correctness of this view.

The second branch, (*e*) *ramus pharyngeus* (*rm. phy.*), given off from the main trunk is very small, and is composed of the fine unstained fibres of the fasciculus-communis component; it was traced to the roof of the pharynx, where fibres were seen to pass down to the end buds. This branch was traced in transverse series, and likewise in sagittal series of larger heads, as far cephalad as the separation of r. palatinus VII. from its ganglion, but in the sagittal sections of the small individual used for reconstruction it could be followed only as far as indicated in Figures 1 and 2.

The third branch of this group, (*f*) *ramus lingualis* (*IX. rm. lng.*), passes ectad, gives off a small motor branch to m. cerato-hyoideus externus, then runs ventrad to the under side of the first epibranchial bar, then curves cephalo-mesiad and is traceable in transverse sections, though not in sagittal ones, to the sense organs of the dorsum of the tongue. The fibres have the same appearance as those of all the other branches of the fasciculus-communis group.

Another branch of fasciculus-communis fibres (*g*) *ramus branchialis* (*rm. brn.*), leaves ganglion IX.+X. immediately caudad of the common trunk of the three branches last described. It appears to give some fine branches to blood-vessels soon after its emergence, but this could not be determined with certainty. The trunk soon divides; the more anterior branch goes to the first and second gills, the posterior to the third gill. It was very difficult to follow the fibres, and their distribution could not be satisfactorily worked out. Minute branches were given off during their course to the gills, but could not be traced to their terminations. A few motor twigs to gill muscles could be distinguished, as they were more deeply stained, and from the posterior branch general cutaneous fibres were seen to pass to the skin. The fine fasciculus-communis fibres were followed to the under side of the gill bars, where they lie close to large blood-vessels, but they could not be traced further. Though their ultimate distribution could not be learned, it seems to me allowable to homologize them with the rami branchiales of the tadpole. Their caudad rather than cephalad course is accounted for by the more posterior position of the gills in Spelerpes.

The last branch from the IX.+X. complex to be described is (*h*) *ramus visceralis* (*X. rm. vsc.*). It has been left in neutral tint to the point of branching, for the same reason that was given for r. hyoideus. It leaves the latero-caudal angle of the ganglion ventral to the lateral-line nerves, and curves ventrad. It is composed of deeply staining and of unstained fibres. Part of the latter are given off in the first branch (*X. rml. vsc. oe.*), which was followed caudad to the region of the oesophagus. Other branches, not plotted in the drawings, were given off mesiad from the region in which the nerve separates into two motor branches (Fig. 1). One of these motor branches (*rm. lar.*) curves cephalad, following closely the course of the hypoglossus for a short distance. It is distributed in part to a transverse sheet of muscles below the pharynx, which Wilder ('91, p. 188) interprets as resulting from a fusion of digastricus pharyngis and dorso-laryngeus. Spelerpes, being a lungless form, has no use for the laryngo-tracheal muscles as such. Wilder maintains that they are employed to form this pharyngo-oesophageal sheet. The distribution of the remaining portion of this branch is to the constrictor arcuum branchiarum. This branch would therefore seem to be r. laryngeus, although it issues from the ganglion with r. visceralis.

The other motor branch (*rm. scap.?*) was traced caudo-ventrad to the region of the shoulder girdle, and is perhaps the r. scapularis of Fürbringer.

G. First and Second Spinal Nerves.

(1) The *first spinal nerve* in Spelerpes bilineatus arises by two ventral roots, which run cephalad a short distance after they emerge from the brain, then pass through the cranial cartilage and divide into two branches, — a dorsal (*rm. d.* $spi._1$), which goes to m. longissimus dorsi, and a ventral (*rm. v.* $spi._1$), which curves caudad, ectad, and then ventrad, finally coming into such close relation with the hypoglossus that the two appear, even when cut transversely, as one nerve. The two remain together for a short distance, then the first spinal curves mesiad and cephalad; it was traced to the mesial surface of m. sterno-hyoideus, but fibres were not seen to actually enter that muscle.

(2) The *second spinal nerve* was found to have a ventral root (*rx. v.* $spi._2$) similar to that of the first, and also a well-developed dorsal root (*rx. d.* $spi._2$). Kingsbury ('95, p. 149) says, "The *hypoglossus* in Amphibia is generally described as formed by the union of the ventral trunks of the two nerves arising immediately caudad of the vagus group, to

which dorsal roots are wanting." He refers, however, to the fact that an indication of a dorsal root for the first spinal was found by Kingsley ('92, p. 678) in Amphiuma and by Mrs. Gage ('93, p. 275) in the larva of Diemyctylus.

In Spelerpes the two roots of the second spinal nerve unite into a ganglion, from which were traced a dorsal (*rm. d. spi.*$_2$) and a ventral branch (*h'gls.*). The former has been represented as entirely motor, because no general cutaneous fibres were actually demonstrated, although the nerve could always be followed to the narrow space between the dorsal muscles and the overlying skin. The ventral branch is the hypoglossus nerve, which runs cephalad and supplies m. sternohyoideus and m. genio-hyoideus.

Von Plessen und Rabinovicz ('91, p. 20) describe the hypoglossus in Salamandra as a branch of the first cervical. No dorsal root was found, but they describe and figure a ganglion connected with the dorsal branch. Kingsley ('92, p. 678) mentions the persistence of the dorsal ganglion as a noticeable feature in connection with the twelfth nerve.

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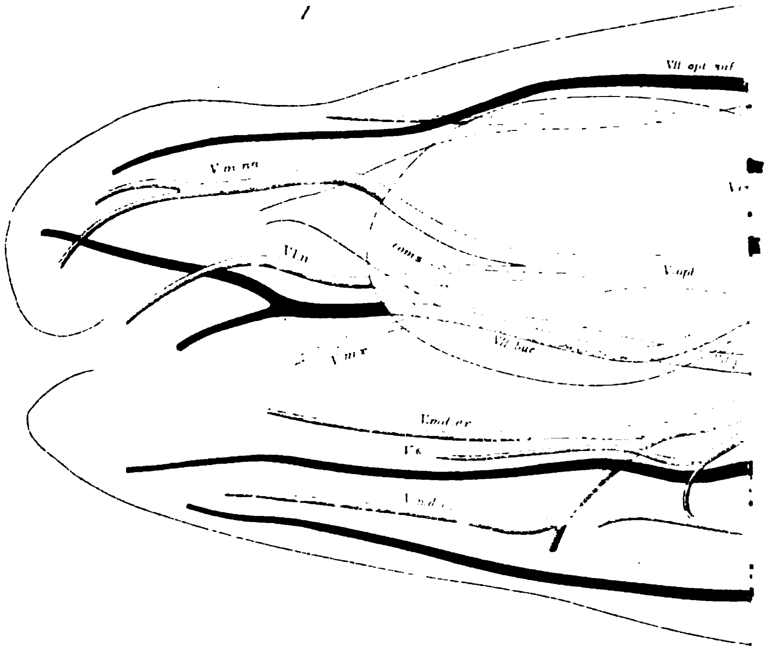

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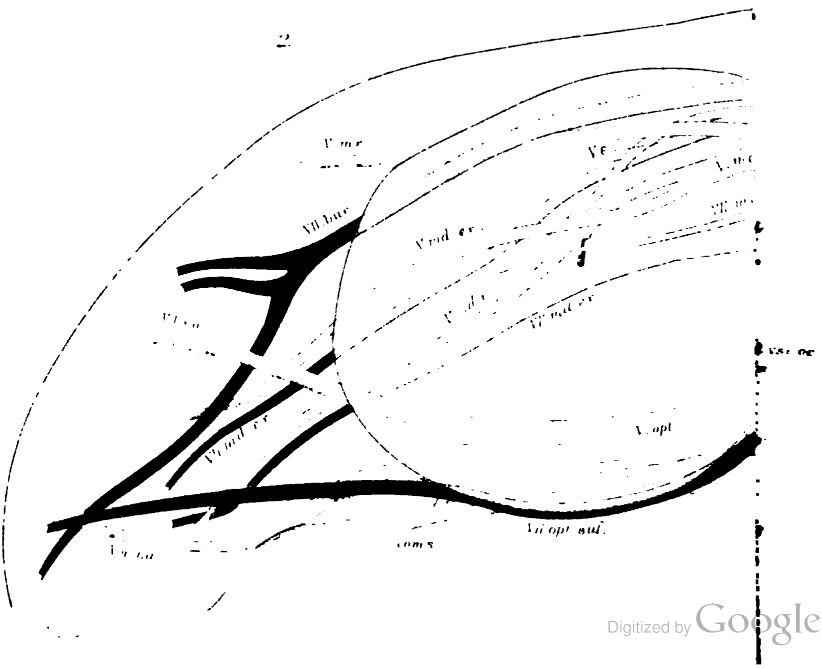

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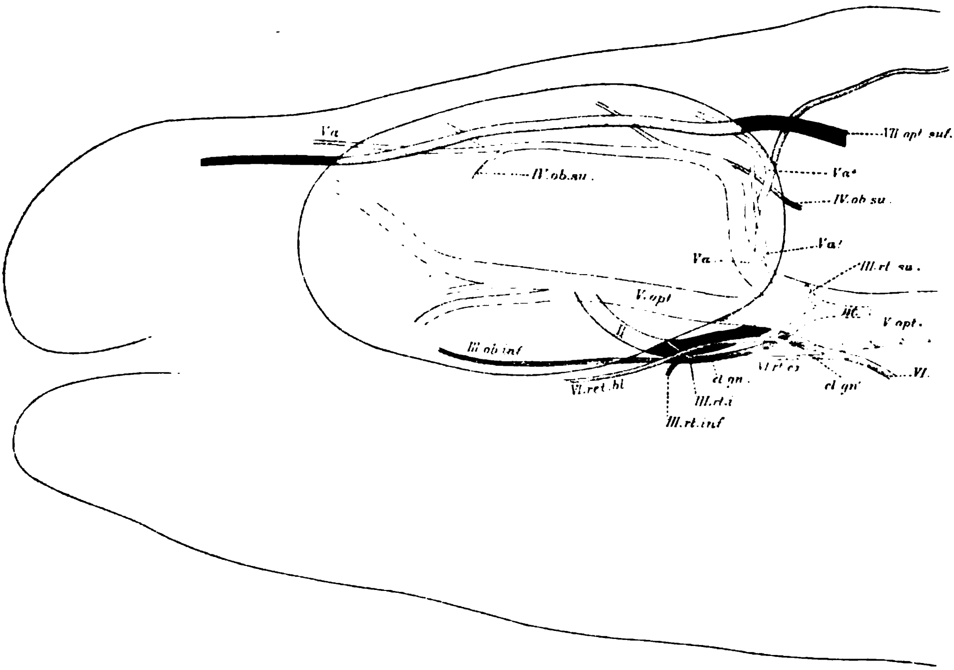
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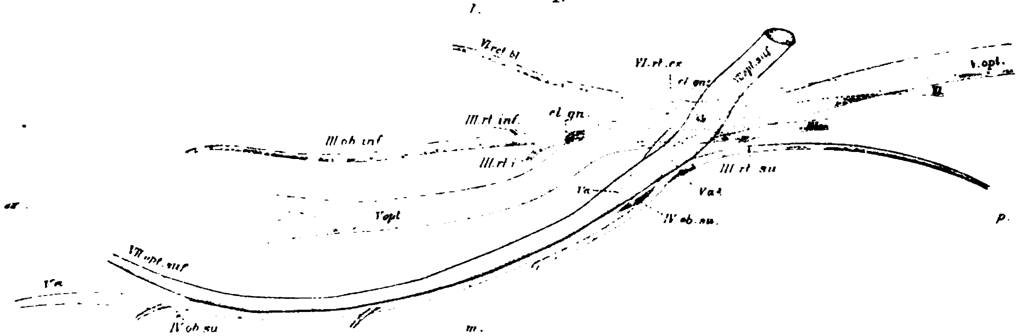
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EXPLANATION OF PLATES.

All figures are reconstruction drawings from sagittal sections of *Spelerpes bilineatus*.

The colors employed follow the scheme adopted by Strong, viz.:

Black for lateral line (also for optic n.),	Pink for fasciculus communis,
Yellow for general cutaneous,	Blue for motor.

List of Abbreviations.

II.	Opticus.
III.	Oculomotorius
III. ob. inf. . .	Branch of III. to m. obliquus inferior.
III. rt. i. . . .	" " " rectus internus.
III. rt. inf. . . .	" " " " inferior.
III. rt. su. . . .	" " " " superior.
IV. ob. su. . . .	Trochlearis to m. obliquus superior.
$V\alpha$	Dorsal branch from ophthalmicus trigemini.
$V\alpha^1$	Small branch of $V\alpha$. (follows m. rectus superior).
$V\alpha^2$	" " " (to skin of dorsum).
$V\beta$	Branch of r. mandibularis *V.* (to m. masseter).
$V\gamma$	" " " " (to m. temporalis).
$V\delta$	" " " " (to skin posterior to angle of jaw).
$V\epsilon$	" " " " (to skin of lower lip).
V. l. n.	Erroneously engraved in Fig. 1 for *V. l. na.*
V. l. na.	Ramus lateralis narium.
V. m. na. . . .	" medialis "
V. md.	" mandibularis trigemini.
V. md. ex. . . .	" " " externus trigemini.
V. md. i. . . .	" " " internus "
V. mx.	" maxillaris trigemini.
V. opt.	" ophthalmicus trigemini.
V. rx.	Ascending root of the trigeminus.
V. rx. mot. . . .	Motor " " "
VI.	Abducens.
VI. ret. bl. . . .	Branch of VI. to m. retractor bulbi.
VI. rt. ex. . . .	" " " rectus externus.
VI. rx. mot. . .	Erroneously engraved in Fig. 1 for *VII. rx. mot.*
VII. buc. . . .	Ramus buccalis facialis.
VII. hoi. . . .	" hyoideus "
VII. hoi-md. . .	" hyomandibularis facialis.
VII. md. ex. . .	Branch of ramus mandibularis externus (or mentalis) facialis.
VII. md. ex.′ . .	" " " " " " " "

VII. md. i. . .	Ramus mandibularis internus (or alveolaris) facialis.
VII. opt. suf. . .	" ophthalmicus superficialis facialis.
VII. pal. . . .	" palatinus facialis.
VII. rx. fas. com.	Fasciculus-communis root of the facialis.
VII. rx. ln. l. . .	Lateral-line root of the facialis.
VII. rx. mot. . .	Motor root of the facialis.
VIII. rx. . . .	Root of auditory nerve.
IX^{1+2}	Anterior root of the ninth cranial nerve.
IX^{3+4}	Posterior " " " "
IX. rm. lng. . .	Ramus lingualis glossopharyngei.
$X.^1 - X.^5$ . . .	Roots of the tenth cranial nerve.
X. rml. vsc. oe. .	Branch of visceralis vagi to the oesophagus.
X. rml. vse. oc. .	Erroneously engraved in Fig. 1 for *X. rml. vsc. oe.*
X. rm. vsc. . . .	Ramus visceralis vagi.
a.	Anterior.
cl. gn.	Ganglionic cells of oculomotorius.
cl. gn.'	" " " abducens.
coms.	Commissure between the r. palatinus VII. and the r. ophthalmicus V.
gn. IX. + X. . .	Ganglion of the glossopharyngeus and the vagus nerves.
gn. ac-fac. . . .	Ganglion acustico-facialis.
gn. Gas.	Gasserian ganglion.
gn. spi.$_2$	Ganglion of second spinal nerve.
h'gls.	Hypoglossus nerve.
l.	Lateral.
m.	Median.
p.	Posterior.
rm. aur.	Ramus auricularis.
rm. brn.	" branchialis.
rm. comn. IX.-VII.	" communicans glossopharyngei ad facialem.
rm. d. spi.$_1$ . . .	Dorsal branch of first spinal. NOTE.—In Fig. 2 the dotted line has been omitted; it should have run to the left and downward from the letters *rm.*
rm. d. spi.$_2$ . . .	Dorsal branch of second spinal.
rm. l.	Ramus lateralis.
rml. amp. a. . .	Ramulus ampullae anterioris.
rml. amp. ex. . .	" " externae.
rml. amp. p. . .	" " posterioris.
rm. lar.	" laryngeus.
rm. phy.	" pharyngeus.
rm. pry.	Erroneously engraved in Fig. 1 for *rm. phy.*
rm. scap. (?) . .	Ramus scapularis (?).
rm. su'tp. . . .	" supratemporalis.
rm. v. spi.$_1$ . . .	Ventral branch of first spinal.
rx. d. spi.$_2$ . . .	Dorsal root of second spinal.
rx. spi.$_1$	Root of first spinal.
rx. v. spi.$_2$ . . .	Ventral root of second spinal.

For the sake of convenience in comparing Fig. 1 with Fig. 3, and Fig. 2 with Fig. 4, Plates 1 and 2 have been bound in *facing* each other.

PLATE 1.

FIG. 1. View of the roots, ganglia, and branches of the cranial nerves of the left half of the head, as if seen from the left side projected on to the sagittal plane. The ear capsule and the eyeball are represented in outline, and the contour of the brain by a line accompanied by a tint on one side of it. × 72.

FIG. 2. Dorsal aspect of the roots, ganglia, and branches of the cranial nerves of the *right* half of the head projected on to the frontal plane. The drawings were made from reconstructions of the *left* half of the head, but in engraving were reversed for the sake of readier comparison with Fig. 4. Outlines of eye, ear, and brain represented as in Fig. 1. × 72.

PLATE 2.

FIG. 3. View of the branches of the cranial nerves in the vicinity of the left eye, seen from the left side, projected on to the median plane, to show especially the eye-muscle nerves in relation to the II. and certain branches of the V. and VII. cranial nerves. × 72.

FIG. 4. Dorsal view of the nerves shown in Fig. 3, but from the *right* side of the head, projected on to the frontal plane. Compare also with Fig. 2. The superficial ophthalmic VII. has been only faintly shaded, instead of being printed in black, in order to allow the course of the underlying nerves to be seen. The distal end of *IV. ob. su.* has not been colored blue, owing to a mistake of the lithographer. × 163.

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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

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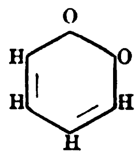
By C. Loring Jackson and Waldemar Koch.

Presented May 9, 1900. Received October 17, 1900.

Attempts to prepare the orthobenzoquinone



have been mentioned, so far as we can find, in only two papers. The first is that by Zincke,† in which he describes tetrabromorthoquinone and tetrachlororthoquinone, but says that a number of attempts to make the unsubstituted orthoquinone have failed to produce the desired result. The second is by Hinsberg and Himmelschein,‡ who obtained orthodioxydiphenylsulphone by the action of potassic dichromate on a mixture of pyrocatechine and benzolsulphinic acid, and draw the inference that the formation of this substance probably was preceded by the formation of orthoquinone. They add that all their experiments to isolate orthoquinone have failed because of its strong tendency to condensation and polymerization.

It seemed to us that one probable cause of the ill success of these experiments was the sensitiveness of the orthoquinone to oxidizing agents; this view was confirmed by the observations of Cousin,§ that trichlorpyrocatechine and dibrompyrocatechine give only red resinous products with

* The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the Degree of Doctor of Philosophy by Waldemar Koch.

† Ber. d. chem. Ges., XX. 1776 (1887).

‡ Ber. d. chem. Ges., XXIX. 2025 (1896).

§ Annales de Chim. et de Phys., [7] XIII. 485.

nitric acid, whereas the trichlor- or tribrom-homopyrocatechine gives under the same conditions an orthoquinone; and also by some experiments undertaken by H. A. Torrey and one of us on the action of hydric dioxide or electrolytic oxygen on pyrocatechine, which led to unpromising black products. Accordingly we searched for a method which would produce a quinone without the use of an oxidizing agent, and found one in the action of iodine on the lead salt of the dioxybenzol. After having shown that the method converted hydroquinone into quinone, we applied it to pyrocatechine; but our first experiments led to no result, because we used alcohol as our solvent, which attacks the orthoquinone as soon as it is formed. Upon replacing the alcohol by chloroform we succeeded in obtaining a dark garnet red solution, in which the presence of orthobenzoquinone was established by a number of tests given later in this paper.

From this solution we next tried to isolate the solid orthoquinone, but after trying every method we could devise, which gave even a remote promise of success, we have failed to obtain a trace of solid orthoquinone, and are forced to the opinion that it cannot exist in the solid state, or even for any length of time in solution. The products obtained in place of the orthoquinone in every case were a black substance insoluble in chloroform, and a brown substance, or mixture of substances, which dissolved in chloroform; this brown product we have not attempted to investigate, but we have studied the black insoluble product, and can give a fairly complete account of its nature in spite of its unmanageable properties. It begins to form in the chloroform solution of the orthoquinone in less than an hour, and is best obtained by allowing the solution to stand in a corked flask for not more than thirty hours. A combustion of the substance gave results corresponding to the formula $C_{12}H_8O_5$; the analysis of a lead salt prepared in a somewhat different way indicated the same formula, and this was confirmed by two analyses made by H. A. Torrey of his product from the electrolytic oxidation of pyrocatechine, which seemed to be identical with ours, and by an analysis of the benzoyl derivative of our black substance; we have, therefore, five analyses of four different samples, all of which agree with each other, and leave no doubt that the substance is a definite compound, and has the formula $C_{12}H_8O_5$. This formula indicates that the compound was formed by the union of two molecules of orthoquinone with the introduction of an additional hydroxyl group, a view which is confirmed by the analysis of the lead salt $C_{12}H_6O_5Pb$, in which there are evidently two benzol rings to each atom of lead. When we consider the manner in which these two benzol rings

are united, two theories seem especially worthy of attention: first, the two rings may be joined directly, so that the compound is a substituted diphenyl, (I.) $O_2(HO)H_2C_6\text{-}C_6H_3(OH)_2$; or second, they may be united by two atoms of oxygen forming a substituted pyrocatechine ether according to this formula: (II.) $(HO)H_2C_6{=}O_2{=}C_6H_2(OH)_2$* The first (diphenyl) formula is rendered much more probable than the second by the analogy between our orthoquinone and the orthonaphthoquinone, which is converted by dilute sulphuric acid into dinaphthyldiquinhydrone,† $O_2H_5C_{10}\text{-}C_{10}H_5(OH)_2$, a black powder like our alteration product; this has been proved by Korn ‡ to be a dinaphthyl body by conversion into α-α dinaphthyl and diphthalylic acid, $(COCO)(C_6H_4COOH)_2$. The support of the diphenyl formula by this analogy is so strong that we should feel it was hardly worth while to consider the second (ether) formula, if it were not for the fact that we have observed an oxygen attachment similar to that in Formula II. in a derivative of tetrabromorthoquinone, described later in this paper. To decide between Formula I. and Formula II. we studied the action of reducing agents on the black substance, as, if it were an ether (Formula II.), it should be reduced to a mixture of pyrocatechine and a trioxybenzol; whereas a diphenyl compound (Formula I.) would only take up two atoms of hydrogen without decomposition.§ We selected as the reducing agent sodium amalgam and water, because this had proved effective in breaking up the pyrocatechine ether containing bromine already alluded to; but, even after long continued action on our black alteration product, not a trace of pyrocatechine could be detected; the only reduction product was a black substance evidently as complex as the original body. This result, therefore, declares decisively in favor of the diphenyl structure (Formula I.).

The action of benzoylchloride on the black substance in presence of sodic hydrate converted it into a tribenzoyl derivative, $C_{12}H_5O_2O_3(COC_6H_5)_3$, thus proving the existence of three hydroxyl groups in the substance; and this benzoyl derivative, and also the original black compound, gave new substances with phenylhydrazine, which contained nitrogen, as was shown by the analyses. Unfortunately the percentage of nitrogen found in both cases was far below that required by the probable formulas, which

* In both these formulas the third hydroxyl group may be attached to the other benzol ring.

† Stenhouse and Groves, Ann. Chem. (Liebig), CXCIV. 205.

‡ Ber. d. chem. Ges., XVII. 3020.

§ Korn did not succeed in splitting dinaphthyldiquinhydrone into simpler bodies by reduction. — Ber. d. chem. Ges., XVII. 3024.

is undoubtedly accounted for by the difficulty in purifying these amorphous and infusible substances; our analyses, therefore, amount only to qualitative proofs of the presence of nitrogen. The introduction of the nitrogen, however, makes it highly probable that both the original substance and its tribenzoyl derivative contain oxygen atoms in the quinone position. We feel justified from the results of the foregoing experiments in assigning to the black alteration product the formula $O_2(HO)H_2C_6$-$C_6H_3(OH)_2$, in which two of the hydroxyl groups are probably in the ortho position to each other, since the substance forms a stable lead salt when treated with plumbic acetate.

We have made no progress toward determining the position of the third hydroxyl group, which may even be attached to the other benzol ring. The introduction of this third hydroxyl group is not without analogy, since the dinaphthylorthoquinone $C_{10}H_5O_2$-$C_{10}H_5O_2$ is converted by the action of the air on its solution in weak alkali into the dioxy compound $C_{10}H_4OHO_2$-$C_{10}H_4OHO_2$.* In our case, however, the oxygen of the air took no essential part in the reaction, as the same alteration product was formed in an atmosphere of carbonic dioxide; and this is not surprising, as we have had frequent occasion to observe that the orthobenzoquinone is a much stronger oxidizing agent than the orthonaphthoquinone, so that one portion of it might easily oxidize the other during the polymerization. The portions of the orthoquinone which gave up oxygen during the formation of the black body were undoubtedly converted into the brown substances soluble in chloroform, which made up about half of the total product.

Although, as has been already stated, we could not obtain the orthoquinone in the solid state, many of its properties can be determined from the study of its solution in chloroform; thus, there can be little doubt that it has an intense red color and little if any odor, as the solution smelt of nothing but chloroform, whereas a smell as strong as that of paraquinone could have been detected even in presence of the amount of chloroform used. Its very slight stability has been dwelt on at sufficient length already, but we should add that it seems to be decomposed at once by even small quantities of water or alcohol.

We turn next to the reactions of the solution on which is based our inference that it contained orthoquinone. Hydrochloric acid converted it into monochlorpyrocatechine, which, however, was mixed with a little pyrocatechine, as would be expected, since Wichelhaus † has shown that

* Korn, Ber. d. chem. Ges., XVII. 3021.

† Ber. d. chem. Ges., XII. 1504.

the action of hydrochloric acid on parabenzoquinone consists in the formation of hydroquinone and chlorine, which subsequently react together, and in this corresponding case part of the pyrocatechine formed could well have escaped the substituting action of the chlorine. Reducing agents like ammonic sulphide or sulphurous dioxide produced pyrocatechine from this chloroform solution. Bromine formed with it tetrabrompyrocatechine, the reduction of the orthoquinone being achieved in this case by the hydrobromic acid formed in making the substituted quinone.

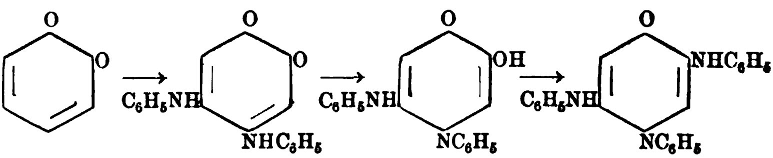
When the chloroform solution was added drop by drop to a solution of benzolsulphinic acid also in chloroform, an orthodioxydiphenylsulphone, $C_6H_5SO_2C_6H_3(OH)_2$, melting at 153° was formed, which should be identical with that obtained by Hinsberg and Himmelschein * by oxidizing pyrocatechine in presence of benzolsulphinic acid, but the properties of the two substances show they are different. Hinsberg and Himmelschein's substance contained water of crystallization, and melted at 117°, if this were not driven off; at 143° to 145° after heating in the steam-bath; and at 164° if completely dried by previous fusion; our compound contained no water, and melted at 153°, whether dried at ordinary temperatures or by previous melting. We have not succeeded in finding the conditions under which Hinsberg and Himmelschein's compound is formed, so that we were unable to compare the two substances, and must consider with our present knowledge that they are isomeric.

With aniline the chloroform solution gave a dianilidoquinoneanil, $C_6H_2(C_6H_5NH)_2O(C_6H_5N)$, which melted at 203°, and by this and a careful comparison of its other physical properties was proved to be identical with the body prepared by Zincke and von Hagen † from paraquinone by the action of aniline and acetic acid. As this substance has previously been made only from paraquinone, it has always been supposed that it contains the oxygen and anil group in the para position to each other, but after our preparation of it from orthoquinone it is also possible that it is a derivative of orthoquinone; and some weight is given to this view by the fact that it is formed easily from the orthoquinone by aniline alone, whereas it can be prepared from the paraquinone only with difficulty, and by the combined action of aniline and acetic acid. On the other hand, it seems hardly prob-

* Ber. d. chem. Ges., XXIX. 2025.
† Ber. d. chem. Ges., XVIII. 785

able that a derivative of orthoquinone would be so stable as this; and the beta-naphthoquinone forms with aniline and alcohol a corresponding anilidonaphthoquinoneanil, $C_{10}H_5O(C_6H_5NH)(C_6H_5N)$, which is undoubtedly a derivative of alpha-naphthoquinone. Zincke * also has obtained recently from the azimidodichlororthoquinone by warming it with aniline an azimidoanilidomonochloroxyparaquinone, and similar cases of conversion of orthoquinones into derivatives of paraquinones are not rare. We are so strongly of the opinion, therefore, that our dianilidoquinoneanil is a para body with the constitution $O, 1. C_6H_5N, 4. (C_6H_5NH)_2, 2. 5$, that we have not thought it worth while to submit the question to an experimental investigation, which would of necessity occupy much time. Assuming that the constitution given above is correct, the body would be formed from the orthoquinone by the following series of transformations, which are modelled after those worked out by C. Liebermann † for the corresponding case of beta-naphthoquinone: —

I. II. III. IV.



The replacement of the two hydrogen atoms of the orthoquinone by the anilido groups to form II. takes place under the oxidizing influence of another portion of the orthoquinone, which takes up hydrogen to form pyrocatechine (always formed in our process); II. then passes by isomerization into III., which is converted into IV. by the further action of aniline.

Upon treating the solution of orthoquinone with orthophenylenediamine no phenazine was formed, but the reaction seemed to consist only in the oxidation of the diamine.

We have also devoted some attention to the study of the tetrabromorthoquinone, and have obtained from it two derivatives. The first of these was prepared by treating tetrabromorthoquinone with tetrabrompyrocatechine dissolved in acetic acid and water; it was a beautiful red

* Ann. chem. (Liebig), CCCXI. 276.
† Ber. d. chem. Ges., XIV. 1664.

body, which was soluble only in warm nitrobenzol. Its formula was $C_{12}Br_6O_4$, and it was formed by the following reaction:

$$C_6Br_4(OH)_2 + C_6Br_4O_2 = C_{12}Br_6O_4 + 2HBr,$$

as was shown by the detection of hydrobromic acid as one of the products of the reaction, and the fact that a good yield was obtained only when the two reagents were used in equal amounts. This formation of the substance is most naturally explained by supposing that the two benzol rings are united together by two of the atoms of oxygen forming a substituted pyrocatechine ether, $C_6Br_4{=}O_2{=}C_6Br_2O_2$, but it is also possible that the union took place directly between the two benzol rings forming a diyhenyl compound with this formula, $O_2Br_3C_6\text{-}C_6Br_3O_2$, the two atoms of bromine removed in this reaction combining with the atoms of hydrogen of the pyrocatechine, and thus oxidizing it so that the body contains two orthoquinone groups. To decide between these two formulas the substance was submitted to reduction with sodium amalgam, as under these circumstances the pyrocatechine ether should be split into two molecules of pyrocatechine, while the diphenyl compound should be reduced without splitting the molecule. The principal product of this reduction was a chocolate brown substance, which contained an amount of bromine nearly identical with that of the original body, and was converted into it again by nitric acid. With it there was always formed a certain amount of pyrocatechine, and this seemed to us strongly in favor of the ether formula, but it could not be considered conclusive, as the amount of pyrocatechine was much less than that of the brown product. In the hope of increasing the yield of pyrocatechine we submitted the brown product again to the action of sodium amalgam, but found it was entirely unaffected; we accordingly oxidized it to the original red body, — a reaction which takes place quantitatively, — reduced this again by sodium amalgam, obtaining fresh quantities of pyrocatechine and the brown body, and continued these alternate reductions and oxidations until the original specimen of the red body had been completely converted into pyrocatechine. Although we could wish that this conversion had taken place by reduction alone, the use of the oxidations cannot be held to vitiate the argument, as they gave a quantitative yield of the original substance, and we feel justified, therefore, in inferring that the two benzol rings are united by two atoms of oxygen, and that the substance is a pyrocatechine ether.

The brown product formed by the action of sodium amalgam was also obtained by the action of tribrompyrogallol on the tetrabromorthoqui-

none, and of hydrochloric acid at 160° to 175° on the red pyrocatechine ether. There seems no doubt, therefore, that it is formed from the red body by the conversion of two orthoquinone oxygen atoms into hydroxyl groups; in other words, that it is the pyrocatechine corresponding to the red orthoquinone; and this view is confirmed by the oxidation of the brown substance to the red by nitric acid. The reaction of the hydrochloric acid is especially instructive in regard to the constitution of these two bodies, as it is the familiar conversion of a quinone to a hydroquinone by this reagent. The red color of the original substance also points to the presence of orthoquino oxygen in it, whereas the lighter color of the reduction product (brown when crystallized, but purplish white when amorphous) confirms the view that it is the hydroxy compound. We therefore assign the following formulas and names to these substances, — red compound, $Br_4C_6{=}O_2{=}C_6Br_2O_2$, hexabromorthoquinopyrocatechine ether; the brown reduction product, $Br_4C_6{=}O_2{=}C_6Br_2(OH)_2$, hexabromdiorthoxypyrocatechine ether. The only observed fact not in accordance with this last formula is that the substance does not dissolve in a solution of sodic hydrate, as we should expect it to do considering that it contains two phenol hydroxyls; this may, however, be explained by the very slight solubility of the substance (soluble only in warm nitrobenzol), which might prevent the solution of sodic hydrate from coming into sufficiently close contact with it to react.

The hexabromorthoquinopyrocatechine ether was formed when acetic acid or alcohol was used as the solvent, but none of it was obtained when the tetrabromorthoquinone and tetrabrompyrocatechine were mixed in solution in chloroform or ether. In this latter case the residue left after the evaporation of the solvent was a reddish white mass, apparently a mixture of the unaltered reagents, which contained none of the hexabromorthoquinopyrocatechine ether. This is strange, as Zincke by mixing the two substances in ethereal solution obtained a black crystalline substance. An attempt will be made in this laboratory next year to find the conditions under which this black compound is formed.

We have succeeded also in obtaining a reaction similar to that just described from tribromresorcine and tetrabromorthoquinone. The other phenols tried acted simply as reducing agents. The product proved to be a ditribrommetoxyphenyldibromorthoquinophenylene ether,

$$(C_6HBr_3OHO)_2C_6Br_2O_2.$$

This substance melts at 217°, and like the reduction product just described, does not dissolve in a solution of sodic hydrate, in spite of the two

phenol hydroxyl groups it contains, according to its most probable formula. We should explain this anomaly in the same way as before, although this substance is much more soluble than the reduction compound.

With glacial acetic acid the tetrabromorthoquinone $C_6Br_4O_2$ formed a white compound, to which we have given much attention, but of which we can only give a very imperfect account. Zincke * in his paper on tetrabromorthoquinone noticed that it was attacked by glacial acetic acid, but did not isolate the product; on the other hand he obtained a white body by crystallizing tetrabromorthoquinone from ether and ligroin, which we have not succeeded in encountering. When tetrabromorthoquinone is evaporated to dryness with glacial acetic acid, a small amount of the red hexabromorthoquinopyrocatechine ether is formed, but the greater part of the quinone is converted into a white crystalline body melting at 230°, the analysis of which led to one of the two following formulas, $C_{14}H_2Br_8O_5$ or $C_{14}Br_8O_5$. The first would be formed by the union of two molecules of the tetrabromorthoquinone with one of acetic acid, one molecule of water being eliminated, thus: —

$$2C_6Br_4O_2+C_2H_4O_2=C_{14}H_2Br_8O_5+H_2O.$$

The second would be formed from the first by removing two atoms of hydrogen, which could be done by the oxidizing action of another portion of the tetrabromorthoquinone, and the tetrabrompyrocatechine thus formed would then give rise to the red body, which always accompanied the white product; but the amount of this red compound always fell far below that which should be formed, if it had taken such an important part in the reaction (10 grams of tetrabromorthoquinone should give 5 grams of the red product, whereas the usual yield was only 0.8 gram), and, as the amount of hydrogen found in the white compound was distinctly larger than should have been given by a body free from that element, we have decided to adopt provisionally the formula $C_{14}H_2Br_8O_5$. We had hoped to settle this question by studying the decomposition products of this substance, but so far it has either been unaffected or completely decomposed by all the reagents we have tried. We hope that in the coming year the study of this body will be completed and the work carried on in various other directions in this Laboratory.

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* Ber. d. chem. Ges., XX. 1777.

Experimental Part.

Action of Iodine on the Lead Salt of Hydroquinone.

These experiments were tried to test the efficacy of this method of making quinones. An aqueous solution of ten grams of hydroquinone was treated with the calculated amount of sodic hydrate in a flask, to which the air had access only through a tube containing an alkaline solution of pyrogallol; to the sodium salt thus formed an aqueous solution of plumbic acetate was added, which gave a white precipitate of the lead salt. As this blackened rapidly on exposure to the air, no attempt was made to filter it, but an alcoholic solution of five grams of iodine was added directly to the precipitate suspended in the liquid, when plumbic iodide was formed, as shown by the appearance of a yellow color. After the reaction seemed to have come to an end, the insoluble substances were filtered out, and the filtrate, which had a strong odor of quinone, extracted with ether. This ether extract left on evaporation yellow crystals with a strong odor of quinone, which under the microscope showed the characteristic form of this substance, and after purification by sublimation melted at 112°–113°, which, although distinctly below the melting point of quinone, 115°.7, is near enough to it to prove in conjunction with the other properties that quinone was formed.

To prove that this quinone was formed by the action of the iodine on the lead salt and not by the oxidizing effect of the air, a specimen of the salt mixed with water was exposed to the air for several hours, until it was thoroughly blackened; upon filtration a red solution was obtained which had no odor of quinone. Extraction with ether did not remove the red color, and on the evaporation of the ether, crystals of hydroquinone were obtained, recognized by the melting point, but no quinone. Upon adding an alcoholic solution of iodine to a similar specimen of the lead salt blackened by exposure to the air, the sharp odor of quinine was observed at once, and a considerable amount of this body was obtained from the filtrate. The method, therefore, is applicable to the production of quinones, but naturally would be used only in cases where oxidation is inadmissible.

We also tried some experiments with iodine and the lead salt of resorcine, but as it was evident that the purification of the product would be a matter of great difficulty, we have postponed the continuation of this work until we have finished the study of pyrocatechine.

ORTHOQUINONE.

Action of Iodine on the Lead Salt of Pyrocatechine, Preparation of a Solution of Orthoquinone.

To prepare the lead salt of pyrocatechine two grams of pyrocatechine dissolved in 150 c.c. of water were added gradually, with constant stirring, to a boiling solution of 7.5 grams of plumbic acetate in 250 c.c. of water. The precipitated lead salt was allowed to settle, filtered out, and washed five times with hot water. It was then dried at 100°, and finely pulverized. It is not advisable to use more than two grams of pyrocatechine at a time in making the lead salt, as with larger amounts it was found to be hard to wash out all the impurities.

Ten grams of this lead salt were thoroughly moistened with chloroform in a 500 c.c. glass-stoppered flask. The salt must be absolutely dry, and the chloroform free from water and alcohol, as these substances decompose orthoquinone. A boiling solution of five grams of iodine in 200 c.c. of chloroform was then added to the lead salt and the whole shaken well for five to ten minutes; after which, upon filtering through a dry Gooch crucible, a garnet red solution of orthoquinone was obtained. The amount of iodine used in this experiment is a little more than half that required by the theory (one molecule to each molecule of the lead salt). This large excess of the lead salt was used to avoid as far as possible the presence of iodine in the chloroform solution, and in this we were fairly successful, as a sample of it, when tested with a fresh specimen of the lead salt of pyrocatechine, showed only a trace of plumbic iodide.

This chloroform solution contained orthobenzoquinone, $C_6H_4O_2$ 1.2, as is proved by the experiments described later in this paper, and it must have been a nearly pure solution of this body, since the only other substance which could have been present was iodine, and the amount of this was very small, as shown in the preceding paragraph. It had a dark garnet red color, and no odor could be perceived except that of the chloroform. Within an hour from the time of its preparation it began to show signs of alteration by depositing a black precipitate, and after twenty-four to thirty hours all the orthoquinone had disappeared from the solution. We have made numerous attempts to isolate the solid quinone from its solution in chloroform, of which the following is a brief summary: Evaporation spontaneously at ordinary temperatures; evaporation at —12°; evaporation *in vacuo* of a solution in pure chloroform made from chloral, so as to avoid all traces of alcohol which decomposes

the orthoquinone; evaporation by a stream of dry air, or dry carbonic dioxide passed through the solution cooled by a freezing mixture; precipitation with ligroin at $-5°$; precipitation with tetrachloride of carbon at $-20°$; we had great hopes of this last attempt, as we had not succeeded in making any of the orthoquinone, when tetrachloride of carbon was substituted for chloroform in the preparation, and we inferred from this that the quinone probably was insoluble in this substance; but this, as well as all the other experiments mentioned above, did not lead to the desired result. The product in every case was the black alteration product already mentioned, the nature of which will be discussed presently, so that we are forced to the conclusion that the orthobenzoquinone cannot exist for any length of time, if at all, in the solid state.

Study of the Alteration Product of Orthobenzoquinone.

This substance was most conveniently obtained by allowing the chloroform solution of orthobenzoquinone, prepared as already described, to stand at ordinary temperatures in a corked flask from twenty-four to thirty hours.* The black precipitate thus formed was not easy to purify, for although it was soluble in alcohol and some other solvents, all our attempts to crystallize it have failed; we finally decided to depend for its purification on its insolubility in chloroform and benzol. Accordingly, after filtering it out from the chloroform in which it was formed, we washed it thoroughly with chloroform, and afterward extracted it three times with hot benzol. About 40 per cent of the orthoquinone used was converted into this black product. In calculating this yield we assumed that the amount of orthoquinone in the chloroform solution corresponded to the amount of iodine used in making it. The black substance, after it had been purified by extraction with benzol, was dried *in vacuo* and analyzed with the following results: —

0.2041 gram of the substance gave on combustion 0.4684 gram of carbonic dioxide and 0.0696 gram of water.

	Calculated for $C_{12}H_6O_2(OH)_2$.	Calculated for $C_{12}H_5O_2(OH)_3$.	Found.
Carbon	66.67	62.07	62.59
Hydrogen	3.70	3.45	3.79

These numbers would indicate that the substance has been formed by the union of two molecules of orthoquinone with the introduction of a

* The solution should not be allowed to stand more than thirty hours, as in that case the product is contaminated with a brown impurity.

hydroxyl group, but it is obvious that the composition of a body like this, which is amorphous, and has no definite melting point, can be determined only by the analysis of several samples prepared by different methods. Accordingly we undertook the preparation and analysis of the lead salt, which should be insoluble and stable, if the substance contains two hydroxyls in the ortho position to each other, as would be the case if it is formed from two molecules of orthoquinone. Further, as we thought that the additional hydroxyl indicated by the analysis might have been introduced by the action of the oxygen of the air, we repeated the preparation in an atmosphere of carbonic dioxide. The solution of orthoquinone was made from the lead salt of pyrocatechine and iodine in a flask filled with this gas, and was separated from the plumbic iodide by means of a rose filter with an asbestos film without exposing it to the air. Upon standing over night still in an atmosphere of carbonic dioxide, a black precipitate was formed identical in appearance with that obtained by the ordinary process. This was purified in the way already described, and then converted into its lead salt as follows: 0.3 gram of this black body dissolved in 40 c.c. of alcohol was added to a boiling solution of one gram of plumbic acetate in 400 c.c. of water; this large amount of water is necessary to prevent the alcohol from precipitating plumbic acetate, which, becoming imprisoned in the lead salt, could hardly be removed by washing. The jet black lead salt thus obtained was washed five times with hot water, dried at 100°, and analyzed with the following result: —

0.2352 gram of the salt gave 0.1645 gram of plumbic sulphate.

	Calculated for $C_{12}H_6O_2O_2Pb$.	Calculated for $C_{12}H_5O_2OHO_2Pb$.	Found.
Lead	49.17	47.39	47.76

This result shows that the oxidizing agent, which introduces the additional hydroxyl, is not the oxygen of the air, but the orthoquinone itself, and this view is confirmed by the fact that the chloroform solution, from which the black compound has separated, contains brown substances probably formed from the orthoquinone in oxidizing the insoluble product, but which were so unmanageable that we were unable to determine their composition.

We would add here two analyses made by H. A. Torrey some years ago in this laboratory with a body agreeing with our black compound in its properties, which he had prepared by the electrolytic oxidation of pyrocatechine. They gave the following results: —

I. 0.1275 gram of the substance gave on combustion 0.2940 gram of carbonic dioxide and 0.0436 gram of water.

II. 0.0608 gram of the substance gave 0.1401 gram of carbonic dioxide and 0.0230 gram of water.

	Calculated for $C_{12}H_5O_2(OH)_3$.	Found. I.	II.
Carbon	62.07	62.88	62.85
Hydrogen	3.45	3.80	4.20

The substance is obviously the same as that previously analyzed, although not so pure.

We have, therefore, four analyses of three samples of this substance prepared or purified in different ways, and, as these agree, there can be no doubt that the black alteration product of the orthoquinone is a definite compound, and has the composition $C_{12}H_8O_5$.

Properties of the Black Alteration Product of Orthobenzoquinone (*Orthodioxyphenyloxyorthoquinone,** $C_6H_3(OH)_2C_6H_2OHO_2$). — It forms an almost black amorphous powder, which does not melt, but decomposes gradually at temperatures above 170°. It is easily soluble in cold alcohol, ether, or glacial acetic acid; insoluble in benzol or chloroform, whether cold or hot. Strong acids have no apparent action on it, but alkalies dissolve it.

The following experiments were undertaken to determine the constitution of the black alteration product.

Reduction of the Alteration Product.

The formula of the substance $C_{12}H_8O_5$ indicates that it contains two benzol rings, and these may either be united directly, forming a diphenyl compound, or they may be united by two atoms of oxygen, forming a substituted pyrocatechine ether, $[C_6H_3OH]O_2[C_6H_2(OH)_2]$. The diphenyl formula, $(HO)O_2H_2C_6\text{-}C_6H_3(OH)_2$, is rendered probable by the formation of the dinaphthyldiquinhydrone † under somewhat similar circumstances from beta-naphthoquinone, which has been proved to be a dinaphthyl compound; ‡ the pyrocatechine ether formula, on the other hand, is in harmony with a derivative of tetrabromorthoquinone, which is described later in this paper. Reduction seemed the easiest way to de-

* This name and formula for the substance are established by the work described later in this paper.

† Ann. Chem. (Liebig), CXCIV. 205.

‡ Ibid. 206. Korn Ber. d. chem. Ges., XVII. 3020.

cide between these formulas, as the ether should be split into pyrocatechine and a trioxybenzol, while the diphenyl product would be reduced without splitting apart the two benzol rings. Upon treating the black alteration product with sodium amalgam and water in an atmosphere of carbonic dioxide for several days, an uninviting black solid was obtained on acidification, which was soaked in water, and this water as well as the acidified filtrate from the reduction extracted with ether, but not a trace of pyrocatechine was obtained. As the bromether, which we have obtained in another part of our work, gives a large quantity of pyrocatechine by this treatment, we infer that the black alteration product is a diphenyl derivative.

Action of Benzoylchloride on the Black Alteration Product.

Half a gram of this substance was dissolved in 10 c.c. of a solution of potassic hydrate (1 : 5), and to the warm solution benzoyl chloride was added drop by drop, until the product of the reaction rose to the surface as an oily mass, leaving the liquid clear. This was then treated with sodic hydrate, in which it did not dissolve, and thoroughly washed with water. The tarry mass thus obtained was dissolved in chloroform, the solution filtered, and the filtrate mixed with an excess of alcohol, which preciptated out the substance. After drying *in vacuo* it was analyzed, with the following result: —

0.2210 gram of the substance gave on combustion 0.5933 gram of carbonic dioxide and 0.0744 * gram of water.

	Calculated for $C_{12}H_6O_3(OCOC_6H_5)_2$.	Calculated for $C_{12}H_5O_2(OCOC_6H_5)_3$.	Found.
Carbon	70.91	72.79	73.21
Hydrogen	3.64	3.68	3.74

The substance is therefore a tribenzoyl compound, and the original black body must have contained three hydroxyl groups. This *benzoxyorthoquino-orthodibenzoxydiphenyl*, $C_6H_2(OCOC_6H_5)O_2C_6H_3(OCOC_6H_5)_2$, † forms a light yellow amorphous powder without a definite melting point. It is easily soluble in chloroform; insoluble in alcohol or water. Alkalies do not dissolve it.

The fact that only three benzoyl groups are taken up by the black alteration product indicates that two of its five atoms of oxygen do not

* A little water was lost in this analysis.

† The distribution of the benzoxy groups in this substance has not been determined.

form part of hydroxyl groups; from the formation of the substance these two atoms of oxygen must either belong to a quinone, or be the connecting atoms of a pyrocatechine ether, and, as our work on the reduction of the alteration product has shown that it is probable they are not pyrocatechine ether oxygen atoms, there can be little doubt that they occur in the quinone configuration, which indeed was the more probable supposition of the two. We tried to confirm this inference by the formation of hydrazones both from the original black alteration product and its benzoyl derivative, but without satisfactory results. When phenylhydrazine in excess was added to a solution of 0.5 gram of the black alteration body dissolved in 10 c.c. of alcohol, the dark blackish color of the solution was discharged, and on pouring the product into acidified water a golden yellow precipitate was formed; but an analysis of the substance gave 6.39 per cent of nitrogen, whereas the most probable formula, $C_{12}H_8O_4NNHC_6H_5$, requires 8.70 per cent of nitrogen. The tribenzoyl derivative of the black substance was dissolved in chloroform, and boiled with an excess of phenylhydrazine for several minutes; a new compound was formed, which was obtained by allowing the chloroform to evaporate spontaneously, treating with an acid to remove the excess of phenylhydrazine, dissolving the residue in cold alcohol, and precipitating the substance from this solution with water. After drying *in vacuo* it was analyzed, and 3.19 per cent of nitrogen found instead of 4.42 per cent of nitrogen required by the formula of the hydrazone, $C_{12}H_5O(NNHC_6H_5)(OCOC_6H_5)_3$. It is evident from these results that phenylhydrazine acts on both of these substances, and that the product in each case contains nitrogen. The results, therefore, as far as they go, confirm our inference that there are two quinone atoms of oxygen in the black substance, but they are of little value, because the exceedingly unmanageable nature of both of these substances prevented us from purifying them sufficiently to determine their composition with certainty.

The work just described establishes the following points with tolerable certainty. The black alteration product is a diphenyl compound, and contains three hydroxyl groups and an orthoquinone group; it may therefore be called orthodioxyphenyloxyorthoquinone, and receive the formula $C_6H_3(OH)_2C_6H_2(OH)O_2$, although the three hydroxyl groups may be attached to the same benzol ring, as we have not determined the position of the third hydroxyl experimentally.

Experiments with the Solution of Orthobenzoquinone.

Action of Hydrochloric Acid on the Solution of Orthobenzoquinone.

Dry hydrochloric acid gas was passed through a fresh chloroform solution of orthoquinone (prepared from iodine and the lead salt of pyrocatechine), until it fumed strongly. After filtering out a slight tarry precipitate, a large part of the chloroform was recovered by distillation, and the concentrated solution thus obtained allowed to stand over night in an open vessel. The residue, which was usually oily, was heated on the steam-bath to drive off the last traces of the solvent and a slight impurity of iodine, and then extracted with a hot mixture of three parts chloroform with one of ligroin, which left behind a large quantity of a black oil. The solution became milky on standing, and deposited an oily substance, followed, when it had cooled, by the formation of crystals. As soon as these crystals began to appear the clear solution was decanted from the oil and allowed to crystallize in a separate vessel. The residual oils by a similar treatment with chloroform and ligroin yielded an additional amount of the crystals. The crystals were dissolved in benzol, and treated with bone-black, after which they were purified by repeated crystallizations from the mixture of chloroform and ligroin. They showed the melting point 84° to 85°, which was not quite constant, indicating that the substance was not perfectly pure; but in spite of this it was dried *in vacuo*, and analyzed with the following result: —

0.2005 gram of the substance gave by the method of Carius 0.1865 gram of argentic chloride.

	Calculated for $C_6H_3Cl(OH)_2$.	Found.
Chlorine	24.57	23.00

This result indicates that the body is monochlorpyrocatechine, but that it contains some pyrocatechine, as would be expected if the reaction ran in the same way as that of hydrochloric acid on parabenzoquinone, since Wichelhaus * has shown that in this case hydroquinone and chlorine are formed in the first instance, and that the substitution compounds, which form the final product, are made by the action of the chlorine on the hydroquinone. We have not attempted to purify the chlorpyrocatechine more thoroughly, as much time and labor would be necessary to obtain sufficient material for this purpose, and the forma-

* Ber. d. chem. Ges., XII. 1504.

tion of chlorpyrocatechine under these conditions is confirmed by the following analysis of the lead salt, made by adding plumbic acetate to an aqueous solution of the product of the reaction of hydrochloric acid on the solution of orthoquinone.

0.3867 gram of the salt gave .03306 gram of plumbic sulphate.

	Calculated for $C_6H_3ClO_2Pb$.	Found.
Lead	58.98	58.55

The monochlorpyrocatechine in the slightly impure state in which we obtained it crystallized in white pearly plates, which are easily soluble in water, alcohol, ether, benzol, chloroform, or acetone; insoluble in ligroin. With an aqueous solution of plumbic acetate it gives a lead salt. It blackens quickly if exposed to the air after treatment with an alkali. The melting point observed by us is of course of no value, on account of the presence of the impurity of pyrocatechine.

Behavior of the Solution of Orthobenzoquinone with Reducing Agents.

Ammonic Sulphide. — Some of the solution of orthoquinone in chloroform was shaken with about one third of its volume of the ordinary laboratory solution of ammonic sulphide. The red color of the orthoquinone disappeared, and the aqueous solution took on a dark color. The two liquids were separated by means of a drop funnel, and the chloroform was extracted twice with water, the extracts being added to the ammonic sulphide solution at first obtained. The mixed aqueous portion was then heated on the steam bath, acidified with hydrochloric acid, allowed to stand until the precipitated sulphur had settled, filtered, and the clear dark colored filtrate extracted with ether. The residue left on the evaporation of the ether was recrystallized twice from benzol, when it was found to melt constant at 103°–104°, and to show all the other properties of pyrocatechine. In order to be certain that the pyrocatechine, detected in the product from the action of ammonic sulphide on the orthoquinone solution, was formed from the orthoquinone, it was necessary to prove that this solution contained no free pyrocatechine; for this purpose a small amount of it taken before the reduction was shaken with water, the water evaporated, and the residue extracted with benzol; the benzol extract was evaporated to dryness, the very slight residue dissolved in water, and tested with plumbic acetate, when it gave no precipitate, showing that no free pyrocatechine was contained in the chloroform solution.

Action of Sulphurous Dioxide. — Dry sulphurous dioxide was passed through the chloroform solution of orthoquinone until it was saturated; the principal product was a black unmanageable precipitate, probably a compound of orthoquinone and pyrocatechine corresponding to chinhydrone; but the filtrate from this left on evaporation crystals, which were recognized as pyrocatechine by their properties and the formation of the lead salt.

Action of Bromine on the Solution of Orthobenzoquinone.

An excess of bromine was added to the solution of orthoquinone in chloroform, the chloroform allowed to evaporate spontaneously, and the crystalline residue, after being heated gently to drive off the excess of bromine, was spread on unglazed porcelain to remove oily impurities. After recrystallization from benzol it showed the constant melting point 191°, which is near enough to 192°–193°, that given by Zincke* for tetrabrompyrocatechine to leave no doubt as to the nature of the substance. For greater certainty the substance was analyzed with the following results: —

I. 0.1835 gram of the substance gave by the method of Carius 0.3210 gram of argentic bromide.
II. 0.1509 gram of the substance gave 0.2637 gram of argentic bromide.

	Calculated for $C_6Br_4(OH)_2$.	Found. I.	Found. II.
Bromine	75.11	74.44	74.39

These numbers are sufficiently near to show that the product of the action of bromine on the orthobenzoquinone is tetrabrompyrocatechine.

Behavior of the Solution of Orthobenzoquinone with Benzolsulphinic Acid.

The chloroform solution of orthoquinone was added drop by drop to a solution of benzolsulphinic acid,† also in chloroform, until the color began to disappear less rapidly, and the solution of the sulphinic acid had assumed a decided reddish tint. After standing over night, the liquid was filtered, the filtrate evaporated to dryness, and the residue allowed to solidify. The solid residue was next treated with hot benzol, which

* Ber. d. chem. Ges., XX. 1777.

† If the conditions were reversed, and the solution of benzolsulphinic acid was added to the solution of orthoquinone, none of the desired sulphone was obtained; we ascribe this difference in behavior to the oxidation of the sulphinic acid by the excess of orthoquinone.

dissolved all but a slight black residue. On allowing the benzol solution to evaporate a crystalline substance was obtained, which was purified by crystallizations with the aid of bone-black at first from water mixed with a little alcohol, finally from water alone, until it showed the constant melting point 153°, when it was dried at 100°, and analyzed with the following results: —

I. 0.2353 gram of the substance gave on combustion 0.4931 gram of carbonic dioxide and 0.0862 gram of water.

II. 0.1454 gram of substance gave by the method of Carius 0.1418 gram of baric sulphate.

	Calculated for $C_6H_3(OH)_2SO_2C_6H_5$.	Found. I.	Found. II
Carbon	57.60	57.14	
Hydrogen	4.00	4.07	
Sulphur	12.80		13.39

As this body must be a substituted pyrocatechine, it should give a lead salt, and upon trying it with a solution of plumbic acetate we obtained one, which was analyzed with the following result: —

0.2601 gram of the substance gave 0.1729 gram of plumbic sulphate.

	Calculated for $C_6H_3O_2PbSO_2C_6H_5$.	Found.
Lead	45.50	45.39

There can be no doubt, therefore, that the substance is a pyrocatechinesulphone or orthodioxydiphenylsulphone.

Properties of Orthodioxydiphenylsulphone, $C_6H_3(OH)_2SO_2C_6H_5$. — It crystallizes from alcohol and water in short, thick, well-formed, white prisms terminated by two planes at an obtuse angle to each other. It contains no water of crystallization, and melts at 153°. It is easily soluble in alcohol, ether, chloroform, or glacial acetic acid; very slightly soluble in cold water, or benzol, freely soluble in either of these liquids when hot; essentially insoluble in ligroin, either hot or cold. Alkalies dissolve it with a yellow color. Ferric chloride gives a bluish green color with it, which changes to red on the addition of sodic carbonate. As has been already mentioned, its aqueous solution gives a precipitate with plumbic acetate.

This substance has the same composition as the orthodioxydiphenylsulphone made by Hinsberg and Himmelschein * by oxidizing pyrocate-

* Ber. d. chem. Ges. XXIX. 2025.

chine in presence of benzolsulphinic acid, and we should expect that the two bodies would be identical, but, strangely enough, they seem to be isomeres, since Hinsberg and Himmelschein's compound contains water of crystallization, and melts in presence of this at 117°; when dried in the steam oven, at 143°–145°; when previously fused in the air, at 164°; whereas our substance contains no water, and melts at 153°, whether dried at ordinary temperatures or by previous fusion. We made five attempts to prepare their body according to Hinsberg and Himmelschein, but did not succeed in finding the conditions under which it is formed, which must lie within very narrow limits; and, as in doing this we had devoted more time to the subject than we could afford, we were obliged to abandon our intention of making a comparative study of the two compounds.

Action of Aniline on the Solution of Orthobenzoquinone.

The solution of orthoquinone in chloroform was heated with an excess of aniline for five minutes on the steam-bath; the chloroform was then allowed to evaporate, and the residue, after having been freed from aniline by treatment with hydrochloric acid and washing with water, was purified by recrystallization from a mixture of two parts of alcohol to one of benzol, until it showed the constant melting point 203°, when it was dried at 100°, and analyzed with the following result: —

0.2909 gram of the substance gave 28.2 c.c. of nitrogen at a temperature of 22° and a pressure of 774 mm.

	Calculated for $C_6H_2(C_6H_5NH)_2C_6H_5NO$.	Found.
Nitrogen	11.51	11.27

The substance is therefore a dianilinoquinoneanil. When the aqueous wash waters obtained in the preparation of this substance were extracted with ether, pyrocatechine was obtained, recognized by its odor and lead salt.

Properties of the dianilinoquinoneanil, $C_6H_2(C_6H_5NH)_2C_6H_5NO$. — Crystallized from alcohol and benzol it forms bronze-colored small needles melting at 203°, although they begin to draw together somewhat at 198°. The melting point of this substance is identical with that (202°–203°) given by Zincke and Hagen * for the dianilinoquinoneanil made from paraquinone by the action of aniline and glacial acetic acid.

* Ber. d. chem. Ges., XVIII. 787.

and, as a comparison of the two substances showed they crystallized in the same form, there can be no doubt of their identity. The formation of a paraquinone derivative from our orthoquinone has been already explained in the introduction to this paper.

In the hope of obtaining a phenazine the solution of orthoquinone was treated with orthophenylene diamine; a reaction took place, the principal products of which consisted of uninviting black substances and pyrocatechine recognized by the formation of its lead salt. From the appearance of the pyrocatechine we inferred that the reaction consisted principally in the oxidation of the diamine by the orthoquinone, and as even after trying the experiment under several varying conditions no more promising results were obtained, this line of work was abandoned. Phenol also gave with the solution of orthoquinone such an uninviting product that we did not attempt to study it. Sodic hydrate gives with the orthoquinone solution a green coloration similar to that obtained by the action of sodic hydrate on tetrabromorthoquinone.

Derivatives of Tetrabromorthobenzoquinone.

The tetrabromorthoquinone used in this work was prepared as follows: 20 grams of pyrocatechine were dissolved in 50 c.c. of glacial acetic acid, and 37 c.c. of bromine added gradually from a burette. The mixture was allowed to stand over night, after which the product was purified by recrystallization from 200 c.c. of glacial acetic acid. In this way forty grams of pyrocatechine yielded 118–126 grams of recrystallized tetrabrompyrocatechine; that is, between 75 and 80 per cent of the theoretical yield. To convert this tetrabrompyrocatechine into tetrabromorthoquinone thirty grams of it were dissolved in 300 c.c. of glacial acetic acid by heating on the water-bath; the solution was then cooled to 16°, or until the glacial acetic acid began to solidify, and eleven grams of fuming nitric acid of specific gravity 1.5 diluted with 60 c.c. of glacial acetic acid added rapidly, the mixture being kept cool and stirred vigorously during the addition; after standing for five minutes 300 c.c. of water were added, and stirred in thoroughly. If the process had run successfully, the tetrabromorthoquinone settled to the bottom in a glistening mass of dark red crystals, which were filtered off, and dried. The product thus obtained melted at 145°–147° instead of 150°–151°, but was pure enough for our work, which was fortunate, as recrystallization from glacial acetic acid is attended by a great loss of material. Thirty grams of tetrabrompyrocatechine gave eighteen grams of tetrabromorthoquinone, which amounts to about 60 per cent of the theoretical yield.

As has just been stated, the crystallization of tetrabromorthobenzoquinone from glacial acetic acid cannot be effected without considerable loss, which we found was due to the conversion of the tetrabromorthoquinone into two new bodies, one of which was red, the other white.* A more careful study of the conditions under which the red body was formed showed us that it was produced by the action of the orthoquinone with tetrabrompyrocatechine, either existing as an impurity in our tetrabromorthoquinone, or formed from it by reduction. After this the study of this red product was carried on with comparatively little difficulty.

Preparation of Hexabromorthoquinopyrocatechine Ether, $C_{12}Br_6O_4$.

Eleven grams of tetrabromorthoquinone and ten grams of tetrabrompyrocatechine were dissolved in 470 c.c. of glacial acetic acid by heating the mixture on the steam-bath, 180 c.c. of water were then added, which produced no immediate precipitate, and the mixture allowed to stand in a warm place for twenty-four hours. During this time a red precipitate was formed, which was filtered out, and washed with hot alcohol to remove unaltered tetrabromorthoquinone and pyrocatechine. In this way 10.7 grams were obtained; that is, somewhat over 60 per cent of the theoretical yield. The purification of the substance offered at first some difficulty because it was insoluble in all the common solvents, but later we found that it dissolved to a limited extent in hot nitrobenzol, and proceeded as follows: Two grams of the crude red body were dissolved in 150 c.c. of nitrobenzol by heating the mixture on the steam-bath (at higher temperatures more of the substance will dissolve, but the solution is attended with decomposition). Upon cooling, the solution deposited about 0.7 gram of crystals, which were submitted to a second similar crystallization from nitrobenzol at 100°, after which the product was extracted several times with hot alcohol to remove adhering nitrobenzol, dried at 100°, and analyzed. As the substance does not melt, we had no means of determining whether this treatment had been an efficient purification.

I. 0.1809 gram of the substance gave on combustion 0.1374 gram of carbonic dioxide and 0.038 gram of water.

II. 0.1008 gram of the substance gave by the method of Carius 0.1637 gram of argentic bromide.

III. 0.1129 gram of the substance gave 0.1843 gram of argentic bromide.

* Zincke (Ber. d. chem. Ges., XX. 1777) observed that acetic acid acted on tetrabromorthoquinone but did not isolate the products of the action.

	Calculated for $C_{12}Br_6O_4$.	Found. I.	II.	III
Carbon	20.93	20.71		
Hydrogen	0.	0.23		
Bromine	69.76		69.13	69.49

Properties of Hexabromorthoquinopyrocatechine Ether. — The substance crystallizes from warm nitrobenzol in short slender prisms of a pure vermilion red color; it does not melt, and is insoluble in all the common solvents; nitrobenzol dissolves it especially when warm, but, if the solution is heated above 100°, decomposition sets in, as shown by a change of color. The ordinary strong acids have no effect on it in the cold, but fuming nitric acid dissolves it with decomposition; alkalies do not dissolve it, but the substance turns black after standing with an alkali for a short time. The red color of the substance indicates that it contains two orthoquinone oxygen atoms, and this view is confirmed by its behavior with hydrochloric acid and reducing agents described later.

The red substance is probably formed from tetrabrompyrocatechine and tetrabromorthoquinone by the following reaction: —

$$C_6Br_4(OH)_2+C_6Br_4O_2=C_6Br_4O_2C_6Br_2O_2+2HBr.$$

To test this a new preparation was made as described above, and, after the mixture had stood twenty-four hours, it was diluted with five times its volume of water, the reddish white precipitate formed filtered out, the aqueous filtrate acidified with nitric acid, and treated with argentic nitrate, when a heavy precipitate of argentic bromide was thrown down, showing the presence of hydrobromic acid among the products of the reaction. It was also found that the best yield was obtained when the two reagents were used in the proportion of equal molecules, as required by the reaction. The best solvent to be used in the preparation was glacial acetic acid and water, as already described, but the red body was also formed in dilute alcohol (the proportions used were 0.5 gram of each reagent, 40 c.c. of alcohol, and 10 c.c. of water). On the other hand, no reaction was observed when the solvent was ether or chloroform. One gram of each of the reagents was dissolved in 50 c.c. of ether (care was taken that the substances were free from even a trace of acetic acid), and allowed to stand twenty-four hours. As no precipitate had formed, the ether was allowed to evaporate spontaneously, when a reddish white residue was left, which looked like a mixture of the unaltered reagents, and dissolved completely in hot chloroform. This showed that none of the hexabromorthoquinopyrocatechine ether had been formed, as it is insolu-

ble in chloroform. Another portion of the residue from the ethereal solution was dissolved in glacial acetic acid, and slightly diluted, when a copious deposit of the red body appeared on standing. The fact that we observed no action when the tetrabromorthoquinone and tetrabrompyrocatechine were mixed in ether is strange, since Zincke * states that by the action of these two bodies in ether or benzol he obtained black shining needles, which changed color at 110° and sintered together to a brownish liquid. We are unable to explain this difference in the results of the experiments, but hope that future work may lead us to the conditions necessary for preparing the black substance.

If the substance is formed by the reaction given above, it is probable that the two benzol rings are connected by two of the atoms of oxygen; but this is not necessarily the case, as the product might also be a derivative of diphenyl, in which both rings contain orthoquinone groups. To settle the mode of union of the two benzol rings, we submitted the substance to reduction with sodium amalgam as follows: Ten grams of the red substance were covered with water in a flask, from which all the air was excluded by a stream of carbonic dioxide, 3 per cent sodium amalgam was then added in large excess, and the reaction was allowed to run at ordinary temperatures in the atmosphere of carbonic dioxide for several days. At the end of this time the red substance had been converted principally into a purplish white body, which seemed to resist the further action of the sodium amalgam; it was, therefore, filtered out, and washed with dilute acid and alcohol; the aqueous filtrate from this substance gave no precipitate on acidification, but on subsequent extraction with ether we obtained from the extract a considerable quantity of a white residue, which after several crystallizations from benzol gave the melting point 100° instead of 104°, the true melting point of pyrocatechine; from the form of its crystals, however, and as it gave the lead salt and the characteristic color with ferric chloride, there can be no doubt that it was pyrocatechine. As has been stated, the principal product of this reduction was the purplish white insoluble substance, the weight of which amounted to 6 grams from 10 grams of the red body; it was obvious, therefore, that no safe inference in regard to the constitution of the red substance could be drawn from the appearance of this small proportion of pyrocatechine. Accordingly, in the hope of increasing our yield of pyrocatechine, this purplish white product was submitted to reduction with sodium amalgam under the conditions used in its formation, the

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* Ber. d. chem. Ges., XX. 1778.

action in this case being allowed to continue for a week, but, as we had reason to expect from our observations in our first reduction, the substance remained essentially unaltered, not more than a trace of pyrocatechine being formed. Meanwhile we had discovered that the purplish white product was converted by nitric acid into the original red substance, and, therefore, we oxidized the unaltered body from the last reduction, and on reducing this again with sodium amalgam, obtained a fresh amount of pyrocatechine with the purplish white product again. By repeating these alternate oxidations and reductions we have succeeded in converting a sample of the red substance completely into pyrocatechine; a result which, it seems to us, proves that this red body is a pyrocatechine ether and not a diphenyl derivative.

The purplish white product of the reduction of hexabromorthoquinopyrocatechine ether by sodium amalgam mentioned frequently in the preceding paragraph proved to have the same solubilities as the mother substance; that is, it was insoluble in all the common solvents except nitrobenzol. It was accordingly recrystallized three times from boiling nitrobenzol, when, as it does not have a definite melting point, it was assumed to be pure. After extraction with alcohol to remove adhering nitrobenzol it was dried at 100°, and analyzed with the following result: —

0.1215 gram of the substance gave by the method of Carius 0.1974 gram of argentic bromide.

	Calculated for $C_{12}Br_6(OH)_2O_2$.	Found.
Bromine	69.56	69.16

Properties. — The substance crystallizes from hot nitrobenzol in very small chocolate brown crystals, which appear to be short, rather blunt needles. As obtained from reduction it has a purplish white color and a characteristic silky lustre. It does not melt at 300°. It is insoluble in all the common solvents except nitrobenzol. An aqueous solution of sodic hydrate does not dissolve it; fuming nitric acid converts it back into the red substance, from which it was made, as is proved by the following experiment: —

Three grams of the chocolate-colored crystals of the reduction product were mixed with 20 c.c. of glacial acetic acid, and 5 c.c. of fuming nitric acid were added. The solid immediately turned red, and, after the mixture had been thoroughly stirred, it was poured into water, and washed.

The oxidation was then repeated in the same way, and the dried product was found to weigh three grams; the conversion from the chocolate-colored substance to the red body, therefore, takes place quantitatively. The red product was recrystallized from warm nitrobenzol, freed from the excess of nitrobenzol with alcohol, dried at 100°, and analyzed with the following result: —

0.1317 gram of the substance gave by the method of Carius 0.2140 gram of argentic bromide.

	Calculated for $C_{12}Br_6O_4$.	Found.
Bromine	69.76	69.15

There can be no doubt that this substance is the hexabromorthoquinopyrocatechine ether described above.

As to the formula of the chocolate-colored product of the reduction there is a certain amount of doubt. Our analysis shows only that its composition does not differ to a marked extent from that of the red mother substance. Its formation by reduction and its conversion to the original body by nitric acid would indicate that it was the hydroxyl compound corresponding to the red quinone, but, on the other hand, its insolubility in sodic hydrate is hard to reconcile with this view. As this may be due, however, to the very slight solubility of the substance in all solvents, which might prevent the sodic hydrate from coming sufficiently in contact with it to react, we are inclined to consider that it is the hexabromorthodioxypyrocatechine ether, and to assign it provisionally the formula $C_{12}Br_6O_2(OH)_2$. We hope that the study of this substance may be finished in this Laboratory in the near future.

Our attempts to decompose the hexabromorthoquinopyrocatechine ether with sulphuric acid led to no result, as no action was observed even after boiling it for several hours with sulphuric acid of 1.44 or even 1.6 specific gravity; but hydrochloric acid reacted upon it, as is shown by the following experiment: 5 grams of the red body were sealed in a tube with 25 c.c. of strong hydrochloric acid, and heated from 160°–175° for five hours; the product, after washing with water and alcohol, showed a strong resemblance to the purplish white body obtained by the reduction with sodium amalgam. On treating it with fuming nitric acid diluted with glacial acetic acid it turned red at once, so that there can be little doubt of the identity of the two substances. This observation can be satisfactorily explained on the theory already adopted, that the purplish white substance is the dihy-

droxy derivative from the red orthoquinone body, as then this action is the familiar reduction of quinone oxygen by hydrochloric acid. This theory is still further supported by the reduction of tetrabromorthoquinone to the purplish white body by tribrompyrogallol described in the next section.

Behavior of Tetrabromorthoquinone with Tribromresorcine.

After we had found, as just described, that tetrabromorthoquinone reacted with tetrabrompyrocatechine, it became of interest to try the action of the tetrabromorthoquinone with other diatomic phenols, and, as we found that unsubstituted phenols of this class reduced the quinone, — pyrocatechine, for instance, reducing it completely to tetrabrompyrocatechine, — we turned our attention to the bromphenols. Of these, tetrabromhydroquinone in alcoholic solution acted only as a reducing agent, giving bromanil and tetrabrompyrocatechine. Tribrompyrogallol also acted only as a reducing agent, giving tetrabrompyrocatechine, which combined with unreduced tetrabromorthoquinone to give the hexabromorthoquinopyrocatechine ether, and this was converted by further action of the tribrompyrogallol into its purplish white reduction product. With tribromresorcine, on the other hand, a new compound was obtained.

8.4 grams of tetrabromorthoquinone and 7 grams* of tribromresorcine † were dissolved with the aid of heat in 600 c.c. of glacial acetic acid mixed with 400 c.c. of water, and allowed to stand for twenty-four hours. At the end of this time a dingy pink precipitate had formed, which was filtered out, washed, and recrystallized from benzol, until it showed the constant melting point 217°, when it was dried at 100°, and analyzed with the following results: —

I. 0.1389 gram of the substance gave by the method of Carius 0.2173 gram of argentic bromide.

II. 0.1370 gram of the substance gave by the method of Carius 0.2144 gram of argentic bromide.

	Calculated for $(C_6Br_3HOHO)_2C_6Br_2O_2$.	Found. I.	II.
Bromine	66.94	66.58	66.61

* The two reagents were used in the proportion of equal molecules, whereas the analysis of the product showed that two molecules of the resorcine should have been taken for each molecule of the quinone.

† The tribromresorcine was prepared by the method of Benedikt (Monatsh. f. Chem. IV. 227.) by mixing the calculated amount of bromine with resorcine dissolved in glacial acetic acid. The product was purified by crystallization from benzol and ligroin.

The substance, therefore, is evidently formed by the union of two molecules of the resorcine with one of the quinone with elimiuation of two molecules of hydrobromic acid, and may be called the ditribrommetoxyphenyldibromorthoquinophenylene ether.

Properties. — It crystallizes from benzol in slender lemon-yellow prisms with square ends, and melts at 217°. It is soluble in ether; slightly soluble in cold alcohol or chloroform, easily soluble in either of these solvents when hot; nearly insoluble in cold benzol, much more soluble in hot benzol, which is the best solvent for it. It does not dissolve in sodic hydrate, which throws some doubt on the formula we have ascribed to it, as this contains two hydroxyl groups.

Action of Glacial Acetic Acid on the Tetrabromorthoquinone.

As has been already stated, tetrabromorthoquinone, when crystallized from glacial acetic acid, is partially converted into a white substance * which we found it convenient to prepare as follows: 10 grams of tetrabromorthoquinone were dissolved in 80 c.c. of glacial acetic acid and the solution slowly evaporated to dryness on the steam-bath, the reddish white residue was moistened with 10 c.c. of glacial acetic, and the slow evaporation on the steam-bath repeated, in order to act on any tetrabromorthoquinone which might have escaped the previous reaction; the residue was then extracted with 200 c.c. of hot alcohol, and filtered boiling, when the red hexabromorthoquinopyrocatechine ether previously described was left behind, as it is insoluble in alcohol. This substance seemed to be a constant product of the reaction, but not a principal one, as the amount was only about 0.8 gram. The alcoholic solution was allowed to cool, and filtered again; then it was diluted with 200 c.c. of water, which precipitated out the white product, amounting to from 5–6 grams. This was purified by crystallization from glacial acetic acid, until it showed the constant melting point 230°, when it was dried at 100°, and analyzed with the following results: —

I. 0.2658 gram of the substance gave on combustion 0.1903 gram of carbonic dioxide and 0.0179 gram of water.

II. 0.1373 gram of the substance gave by the method of Carius 0.2306 gram of argentic bromide.

* Zincke (Ber. d. chem. Ges. XX. 1777) converted tetrabromorthoquinone into a white substance by crystallizing it from a mixture of ether and ligroin. On repeating the experiment we did not succeed in finding the conditions under which the white product is formed.

III. 0.3015 gram of the substance gave on combustion 0.2090 gram of carbonic dioxide and 0.0223 gram of water.
IV. 0.1265 gram gave 0.2122 gram of argentic bromide.
V. 0.1279 gram gave 0.2147 gram of argentic bromide.
VI. 0.1138 gram gave 0.1911 gram of argentic bromide.
VII. 0.1229 gram gave 0.2074 gram of argentic bromide.

	Found.						
	I.	II.	III.	IV.	V.	VI.	VII.
Carbon	19.53		18.90				
Hydrogen	0.75		0.82				
Bromine		71.45		71.39	71.44	71.48	71.83

Of these analyses I. and II. were of samples prepared and purified as described; III. to VII. were of specimens prepared earlier in our work, and in some cases purified by slightly different, and perhaps less effective, methods.

Two determinations of the molecular weight were made by the method of freezing, the solvent being benzol.

I. 0.262 gram of the substance dissolved in 16.58 grams of benzol produced a depression of 0.099°.
II. 0.594 gram of the substance in 16.58 grams of benzol produced a depression of 0.219°.

	I.	II.
Molecular Weight	782	802

The most probable formula to be derived from these data is $C_{14}H_2Br_8O_5$, formed by the union of two molecules of tetrabromorthoquinone with one of acetic acid, one molecule of water being eliminated. The results, however, agree almost as well with $C_{14}Br_8O_5$, although the percentage of hydrogen found is high for a substance which is free from this element. A compound with the formula $C_{14}Br_8O_5$ would be formed by the removal of two atoms of hydrogen from the preceding compound, a reaction which might easily be brought about by the oxidizing action of a portion of the tetrabromorthoquinone; the tetrabrompyrocatechine thus formed in turn acting on the unaltered quinone would give the red body which, as already stated, is always produced with the white substance; but it should be remembered that the quantity of the red body formed is far below that which would be expected from such a reaction.

	Calculated for $C_{14}H_2Br_8O_5$.	Found. I.	II.	Calculated for $C_{14}Br_8O_5$.
Carbon	18.88	19.53		18.92
Hydrogen	0.22	0.75		
Bromine	71.95		71.45	72.07
Molecular Weight	890	782	802	888

It is obvious that the decision can be made between these formulas only by the chemical study of the substance, but unfortunately we have not succeeded as yet in decomposing it by any of the reagents we have tried, so that we must leave this question undecided for the present, with the statement that we consider the formula $C_{14}H_2Br_8O_5$ the most probable. The study of the substance will be continued in this Laboratory next year.

Properties of the Substance $C_{14}H_2Br_8O_5$. — When crystallized from glacial acetic acid it forms small, almost square rhombic plates with a pearly lustre, which melt at 230°. It is easily soluble in ether, benzol, chloroform, acetone, or ethyl acetate; almost insoluble in glacial acetic acid, but its solubility is increased by heat, as the boiling acid takes up from two to three per cent of the substance. Its solubility in ethyl alcohol is similar to that in glacial acetic acid; curiously enough, when first formed, the crude mass is rather freely soluble in alcohol, but, as the purification continues, it becomes less and less so, until, when pure, it is nearly insoluble in cold alcohol, as already stated. It is essentially insoluble in ligroin or in water, hot or cold. The best solvent for it is glacial acetic acid. None of the strong acids dissolve it when cold; nor does even a hot solution of sodic hydrate show any perceptible action with it.

This substance is decidedly stable, as is shown by the following experiments, which were tried in the hope of decomposing it into simpler bodies, in order to throw some light on its nature: 0.5 gram of the white substance were treated with sodium amalgam and water in an atmosphere of carbonic dioxide for eight days. At the end of this time the substance was recovered unaltered, as shown by its melting point. The filtrate was acidified, and extracted with ether, but yielded no pyrocatechine. 0.2 gram of the substance were dissolved in boiling glacial acetic acid, and mixed with 5 c.c. of fuming nitric acid also diluted with glacial acetic acid; no visible reaction took place, and upon dilution with water the original substance was obtained, as shown by the melting point. 0.2 gram were dissolved in cold chloroform, and 3 c.c. of bromine added; after standing for twenty-four hours the chloroform was evaporated,

leaving the original substance, as shown by the melting point. 0.2 gram of the substance were dissolved in benzol, and an excess of aniline added; after standing for twenty-four hours the benzol and aniline were removed, when the unaltered substance was obtained, as shown by the melting point. Phenylhydrazine gave a similar negative result. No action could be observed when the substance was treated with an alkaline solution of potassic permanganate, or was boiled with sulphuric acid of specific gravity 1.44 or 1.6, or heated to 150° in a sealed tube with hydrochloric acid. If it was heated to 250° with hydrochloric acid, the compound was completely destroyed, and complete destruction also ensued when it was treated with fuming nitric acid, or a solution of chromic anhydride, or when it was fused with potassic hydrate. In continuing this work next year renewed attempts will be made to obtain decomposition products of the substance, and efforts will also be made to throw light on its constitution by preparing allied compounds.

It should also be mentioned that acetacetic ester converts tetrabromorthoquinone into tetrabrompyrocatechine, which then forms hexabromorthoquinopyrocatechine ether with unaltered tetrabromorthoquinone. Chloral showed no action with tetrabromorthoquinone even at 100°. The study of the little-known and very reactive tetrabromorthoquinone will be continued in various directions in this Laboratory.

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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY
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ON THE ACTION OF SODIC SULPHITE ON TRIBROMDINITROBENZOL AND TRIBROMTRINITROBENZOL.

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By C. Loring Jackson and Richard B. Earle.

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In the course of an extended study of the action of various reagents on tribromdinitrobenzol (Br_3 1 . 3 . 5 . $(NO_2)_2$ 2 . 4 .) it became of interest to determine whether this substance could be converted into a sulpho-acid by the method of Strecker,* that is, boiling the halogen compound with an aqueous solution of normal sodic sulphite, and experiments in this direction were tried rather early in the work, with negative results. Upon returning to the subject later we did not find any conditions under which an aqueous solution of sodic sulphite acted on tribromdinitrobenzol, but when we substituted alcohol for water as the solvent, we obtained a reaction. This, however, took a different direction from that which we had expected, as under these conditions the sodic sulphite acts as a reducing agent, converting the tribromdinitrobenzol into dibromdinitrobenzol by replacing one of the atoms of bromine by hydrogen. The atom of bromine replaced is the one between the two nitro groups, since the dibromdinitrobenzol formed melted at 117°, which is the melting point of the dibromdinitrobenzol † $Br_2$1.3.$(NO_2)_2$4.6. That the product had this constitution was confirmed by its conversion into the bromanilidodinitrobenzol, which showed the melting point 157°. ‡ Tribromtrinitrobenzol undergoes a similar reduction with an alcoholic solution of normal sodic sulphite, the product being dibromtrinitrobenzol, which can have only this constitution: Br_2 1 . 3 . $(NO_2)_3$ 2 . 4 . 6. It is a new substance, and melts at 135°.

* Ann. Chem. (Liebig), CXLVIII. 90.

† Koerner, Gazz. Chim., 1874, 305.

‡ Jackson and Cohoe, These Proceedings, XXXVI. 75.

In the hope of finding an easier method for making this dibromtrinitrobenzol the action of dibromdinitrobenzol ($Br_2\,1.3.(NO_2)_2\,4.6$) with nitric and sulphuric acids was studied. This gave the desired dibromtrinitrobenzol, but the product was mixed with so large a proportion of tribromdinitrobenzol that the method was not adapted to the preparation of the substance. This tribromdinitrobenzol is a new substance, melting at 150°. There can be no doubt that its constitution is $Br_3\,1.2.3.(NO_2)_2\,4.6$, since it is made by introducing a third atom of bromine into the dibromdinitrobenzol $Br_2\,1.3.(NO_2)_2\,4.6$, and, if this occupied the only other vacant place (5), the product would be the common tribromdinitrobenzol, which melts at 192°. The formation of this tribromdinitrobenzol during this reaction is strictly according to the analogy of the behavior of the tribromdinitrobenzol, which, when boiled with a mixture of fuming nitric and sulphuric acids, gives rise to tribromtrinitrobenzol and tetrabromdinitrobenzol. *

As neither of the new substances just described can be prepared easily on a large scale, we have confined our work on them to the study of the principal action of sodic ethylate on each. This reaction runs in a normal way, giving styphnic diethylether,

$$C_6H(NO_2)_3(OC_2H_5)_2, \quad ((OC_2H_5)_2\,1.3.(NO_2)_3\,2.4.6),$$

with dibromtrinitrobenzol, recognized by its melting point 121°; and with tribromdinitrobenzol a new bromdinitroresorcine monoethylether melting at 78°. The subject did not promise to be of sufficient interest to make it worth while to study the secondary products of these reactions.

Experimental Part.

Action of Sodic Sulphite in Alcoholic Solution on Tribromdinitrobenzol.

Five grams of symmetrical tribromdinitrobenzol ($Br_3\,1.3.5.(NO_2)_2\,2.4$) were dissolved in 70 c.c. of alcohol mixed with 20 c.c. of benzol, five grams of normal sodic sulphite added, and the mixture boiled for five hours in a flask with a return condenser. The red liquid thus obtained was filtered from the insoluble portion, evaporated to dryness, and the residue washed with water, until the yellow color was removed. The part insoluble in water was then recrystallized from alcohol with the aid of bone-black, until it showed the constant melting point 117°. This melting point indicated that it was Koerner's dibromdinitrobenzol †

* Jackson and Wing, These Proceedings, XXII. 139

† Gazz. Chim., 1874, 305.

(Br_2 1 . 3, $(NO_2)_2$ 4 . 6 .), and this was confirmed by treating it with aniline in the cold, when it was converted into the bromanilidodinitrobenzol,* $C_6H_2Br(C_6H_5NH)(NO_2)_2$, recognized by its melting point 157°. For greater certainty the dibromdinitrobenzol was dried at 100°, and analyzed with the following results: —

I. 0.3277 gram of the substance gave 24.6 c.c. of nitrogen at a temperature of 18°.5 and a pressure of 760.3 mm.

II. 0.3195 gram of the substance gave by the method of Carius 0.3707 gram of argentic bromide.

	Calculated for $C_6H_2Br_2(NO_2)_2$.	Found. I.	II.
Nitrogen	8.59	8.65	
Bromine	49.38		49.08

The sodic sulphite, therefore, has removed the atom of bromine standing between the two nitro groups in the tribromdinitrobenzol, and replaced it by hydrogen.

That this was not the only action of the sodic sulphite was shown by the marked yellow color of the products of the reaction. The yellow substance was soluble in water, but, in spite of its strong color, was present in such small quantity that we could not isolate it from the other substances soluble in water, which consisted of sodic bromide and unaltered sodic sulphite. It was undoubtedly the sodium salt of a phenol formed by a secondary reaction.

Action of Sodic Sulphite in Alcoholic Solution on Tribromtrinitrobenzol.

Ten grams of symmetrical tribromtrinitrobenzol (Br_3 1 . 3 . 5 . $(NO_2)_3$ 2 . 4 . 6) were dissolved in 120 c.c. of common alcohol with the assistance of 30 c.c. of benzol, ten grams of normal sodic sulphite added, and the mixture boiled for four hours in a flask fitted with a return condenser. The reaction seemed to run as in the case of the tribromdinitrobenzol, except that it took place more easily, since the red color appeared more quickly. The red solution was filtered, the filtrate evaporated to dryness. and the residue washed with water, after which it was recrystallized from a mixture of alcohol and benzol with the assistance of bone-black, until it showed the constant melting point 135°, when it was dried at 100°, and analyzed with the following results: —

* Jackson and Cohoe, These Proceedings, XXXVI. 75.

I. 0.2384 gram of the substance gave 25.1 c.c. of nitrogen at a temperature of 25° and a pressure of 753.3 mm.

II. 0.2887 gram of the substance gave by the method of Carius 0.2910 gram of argentic bromide.

	Calculated for $C_6HBr_2(NO_2)_3$.	Found. I.	II.
Nitrogen	11.36	11.65	
Bromine	43.10		42.89

The substance is, therefore, dibromtrinitrobenzol (Br_2 1.3.$(NO_2)_3$2.4.6), formed by the replacement of one atom of bromine in the tribromtrinitrobenzol by hydrogen, and the sodic sulphite has behaved like a reducing agent in this case just as it did with the tribromdinitrobenzol.

Properties of Metadibrom-s-trinitrobenzol. — It crystallizes from benzol — or better, a mixture of benzol and ligroin — in broad prisms terminated by two planes at a slightly acute angle to each other, or in slender, blunt-ended prisms, or in rhombic crystals. It has a pale yellow color with a slight greenish tinge, and melts at 135°. It is freely soluble in benzol or ether; soluble in chloroform, acetone, or cold alcohol, freely soluble in hot alcohol; slightly soluble in hot ligroin; insoluble in water. The best solvent for it is a mixture of alcohol and benzol, or of benzol and ligroin; strong hydrochloric or sulphuric acid has no action on it, either hot or cold. Strong nitric acid does not dissolve it in the cold, but forms a yellow solution with it when hot, which deposits the unaltered substance on cooling. Sodic hydrate solution gives a pale yellow solution when hot; no perceptible action when cold. Alcoholic sodic hydrate gives a deep red color.

The aqueous wash waters obtained in the preparation of dibromtrinitrobenzol by this process, although showing a strong red color, contained so little organic matter that we did not succeed in isolating any new compound from them. The residue left on evaporating them consisted chiefly of sodic bromide and unaltered sodic sulphite.

Preparation of Dibromtrinitrobenzol from Dibromdinitrobenzol.

In the hope of finding an easier method of preparing the dibromtrinitrobenzol we next tried to make it from dibromdinitrobenzol. The dibromdinitrobenzol was made by the method of Jackson and Cohoe,* which, however, we modified somewhat in converting the bromacetanilid

* These Proceedings, XXXVI. 77.

into dibromacetanilid, — the monobromacetanilid was mixed with enough glacial acetic acid to convert it into a semi-liquid mass, to which the calculated amount of bromine was added from a burette. It was then warmed on the steam-bath, until it was transformed into a clear, dark-red liquid, which was poured into water, filtered, and the precipitate ground in a mortar with a solution of sodic hydrate to remove the excess of bromine. The dibromdinitrobenzol used for our work was recrystallized until it showed the correct melting point 117°.

To convert the dibromdinitrobenzol into dibromtrinitrobenzol we proceeded as follows. Twenty grams of dibromdinitrobenzol were added to 500 c.c. of fuming nitric acid of specific gravity 1.50 and 200 c.c. of sulphuric acid of specific gravity 1.86, and the mixture was boiled violently for about three hours in a flask closed with a porcelain crucible. Toward the close of the operation a reddish oil separated, after which the process was continued only so long as the liquid boiled freely, since decomposition and darkening of the color resulted from too long continued boiling. After the mixture had been boiled for a sufficiently long time, it was allowed to cool, poured into ice water, and filtered. The precipitate was recrystallized from a mixture of alcohol and benzol, until it showed a constant melting point, but, as this stood at 150°, the substance was not the expected dibromtrinitrobenzol, which melts at 135°. On examining the mother liquors from this substance, however, we found the dibromtrinitrobenzol, which, after purification by crystallization from a mixture of benzol and ligroin, was recognized by its melting point 135°, and the following analysis of the substance dried at 100°: —

0.2174 gram of the substance gave by the method of Carius 0.2203 gram of argentic bromide.

	Calculated for $C_6HBr_2(NO_2)_3$.	Found.
Bromine	43.10	43.10

The dibromtrinitrobenzol is therefore formed by this process, but so much of the other product melting at 150° is formed at the same time that this is not a convenient method of preparing it, and the dibromtrinitrobenzol remains a not easily accessible substance.

Tribromdinitrobenzol, $C_6HBr_3(NO_2)_2$. (Br_3 1. 2. 3. $(NO_2)_2$ 4. 6.).

The substance melting at 150°, prepared by the action of nitric acid and sulphuric acid on dibromdinitrobenzol as described in the preceding section, was dried at 100°, and analyzed with the following results: —

I. 0.2973 gram of substance gave according to the method of Carius 0.4138 gram of argentic bromide.

II. 0.2987 gram of substance gave 0.4150 gram of argentic bromide.

	Calculated for $C_6HBr_3(NO_2)_2$.	Found. I.	II.
Bromine	59.26	59.24	59.13

The substance is, therefore, a tribromdinitrobenzol, and its appearance is not unexpected, since J. F. Wing and one of us * found that tetrabromdinitrobenzol was always formed during the preparation of tribromtrinitrobenzol from tribromdinitrobenzol. There can be no doubt about the constitution of this tribromdinitrobenzol, because it is made from the dibromdinitrobenzol (Br_2 1. 3. $(NO_2)_2$ 4. 6) by the introduction of an atom of bromine, which can enter only in two places, — between the nitro groups, or between the atoms of bromine. If the substitution takes place between the nitro groups, there must be formed symmetrical tribromdinitrobenzol, which melts at 192°; there is left, therefore, for our substance melting at 150° only the constitution Br_3 1. 2. 3. $(NO_2)_2$ 4. 6.

Properties of the 1. 2. 3. *Tribrom*-4. 6. *dinitrobenzol.* — Yellowish white rectangular plates bevelled on the sides, when crystallized from a mixture of alcohol and benzol. Melting point 150°. It is freely soluble in benzol, or ether; soluble in chloroform, glacial acetic acid, or acetone; soluble in cold alcohol, freely soluble in hot alcohol; slightly soluble in cold ligroin, soluble in hot; insoluble in water. The best solvent for it is a mixture of alcohol and benzol. Strong hydrochloric or sulphuric acid gives no visible action hot or cold. Strong nitric acid appears not to act in the cold, but dissolves it when hot, depositing the unaltered substance as it cools. A solution of sodic hydrate does not act on it apparently either hot or cold, but in presence of alcohol gives a light yellow color.

Action of Sodic Ethylate on Dibromtrinitrobenzol.

1.5 grams of dibromtrinitrobenzol (Br_2 1 . 3 . $(NO_2)_3$ 2 . 4 . 6) were dissolved in 15 c.c. of benzol, and mixed with sodic ethylate in the proportion of three molecules of the ethylate to each molecule of the dibrom compound. The sodic ethylate was prepared by adding the calculated amount of sodium to 30 c.c. of absolute alcohol. The liquid at once took on an intense red color, and became turbid. To make sure of completing the reaction the mixture was allowed to stand for twelve hours at ordinary temperature in a cork flask, after which it was filtered, and the

* These Proceedings, XXIII. 139.

filtrate allowed to evaporate spontaneously; the residue was washed with water until the washings were colorless, and then recrystallized from alcohol until it showed a constant melting point, which was found to be 121°. The melting point of styphnic ethylether,

$$C_6H(OC_2H_5)_2(NO_2)_3 \quad (OC_2H_5)_2\,1.3.(NO_2)_3\,2.4.6,$$

is given as 120°.5, and it is described as forming long plates, which quickly turn orange-brown in the light; our substance crystallized in prisms connected by their longer sides, and turned brown by exposure to the light. It contained no bromine. There can be no doubt, therefore, that the two bodies are identical, and that this styphnic ether formed by replacing each bromine by an ethoxyl group is the principal product of the reaction. It was not, however, the only product of the action of sodic ethylate on dibromtrinitrobenzol, as the reaction product insoluble in the organic solvents but soluble in water gave tests for nitrite as well as bromide, and the aqueous washings were colored; but the amount of these secondary products was so small that they could not have been studied without preparing the mother substance on a very large scale, and the importance of the subject did not warrant the great expenditure of time which would have been necessary for this purpose.

Action of Sodic Ethylate on Adjacent Tribromdinitrobenzol.

Seven grams of the tribromdinitrobenzol ($Br_3\,1.2.3.(NO_2)_2\,4.6$) were dissolved in 70 c.c. of benzol, and mixed with sodic ethylate in the proportion of three molecules of the ethylate to each molecule of the tribromdinitrobenzol. The sodic ethylate was prepared by adding the calculated amount of sodium to 70 c.c. of absolute alcohol. A deep red turbid solution was formed immediately, which was allowed to stand in a corked flask at ordinary temperatures for two days, and then filtered, the filtrate allowed to evaporate spontaneously, and the residue washed with water, until the washings were colorless. The portion insoluble in water after recrystallization from alcohol showed the constant melting point 58°, and crystallized in long white needles turning yellow in sunlight, but was formed in such small quantity that there was not enough for analysis; we, therefore, sought the principal product of the reaction in the portion soluble in water. The precipitate formed during the action of the sodic ethylate was dissolved in water, and mixed with the wash waters, which had previously been concentrated to a convenient bulk. The solution was then acidified with acetic acid, which threw down a black tarry precipitate. This was filtered out, washed, suspended in water, and dissolved by adding sodic hydrate to neutralization;

the solution was filtered, and treated with baric chloride, which produced at once a mass of shining yellow needles. These were filtered out, washed with water, and recrystallized several times from alcohol; after which they were dried at 100°, and analyzed with the following results:

I. 0.3636 gram of the substance gave 0.1108 gram of baric sulphate.

II. 0.3071 gram of the substance gave 21.2 c.c. of nitrogen at a temperature of 22°.5 and a pressure of 765 mm. The substance was mixed with a large excess of a mixture of eight parts of fused plumbic chromate with one of potassic dichromate. It was necessary to heat very gradually to avoid too rapid an evolution of the nitrogen.

	Calculated for $[C_6HBr(NO_2)_2(OC_2H_5)O]_2Ba$.	Found. I.	II.
Barium	18.33	17.91	
Nitrogen	7.47		7.86

The substance is, therefore, the barium salt of a bromdinitroethoxyphenol. We have not determined the constitution of this substance experimentally, but there can be little doubt that it is a derivative of resorcine, as the two bromine atoms in the meta position to each other are also in the para and ortho positions to the nitro groups, and this has been shown to be the position most favorable to replacement; whereas the third atom of bromine, which is in the meta position to the two nitro groups, would be replaced with difficulty according to all previous work on this subject; we have no hesitation, therefore, in calling this substance the bromdinitromonoethylether of resorcine.

Properties of the Barium Salt. — It crystallizes from alcohol in fine yellow needles. It is nearly insoluble in water, whether hot or cold, but soluble in alcohol. It is stable at 100°, but if heated suddenly to a high temperature it explodes. Acetic acid does not decompose it.

The free bromdinitromonoethylether of resorcine was obtained by heating the barium salt with an acid; after crystallization from alcohol it melted constant at 78°. It forms long white feathery needles, which turn yellow on standing.

The experiments just described make it highly probable that the substance melting at 58° and insoluble in water is the bromdinitroresorcinediethylether. There were also other products of the reaction, as the soluble salts obtained gave a test for nitrite as well as for bromide, but they were formed in such small quantity that it did not seem to us worth while to undertake the study of them.

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FALSE SPECTRA FROM THE ROWLAND CONCAVE GRATING.

By Theodore Lyman, Ph.D.

With a Plate.

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FALSE SPECTRA FROM THE ROWLAND CONCAVE GRATING.

BY THEODORE LYMAN.

Presented October 10, 1900, by W. C. Sabine. Received October 26, 1900.

It is proposed to show in the following paper that among the spectra formed by the Rowland concave gratings there are spectra not accounted for by the ordinary theory of the grating; that such spectra are common, and at times fairly strong and of excellent definition; that these spectra are diffraction spectra, of much less dispersion than the ordinarily recognized spectra, and that the errors of ruling to which they are due are not local, but general to the whole surface of the grating. Finally, it is proposed to explain an experimental method by which these false lines can be sorted out from the regular and calculable overlapping spectra. These lines are especially dangerous in series spectra work, giving a somewhat systematic reproduction of strong lines and groups, which reproductions in actual vibration frequencies do not exist. There is probability and some evidence that such errors have been committed in the past, and it was in the presence of this danger that the false spectra were here discovered.

In the year 1893, Schumann showed that the ultra-violet spectrum could be extended to the neighborhood of 1000 μ. He used a spectroscope fitted with a fluorite prism and fluorite lenses. The apparatus was so constructed that it could be enclosed in a case from which the air could be exhausted. According to his investigation, it was chiefly the absorption of the air for light of very short wave lengths that had prevented other investigators from extending the spectrum below wave length 1800 μ. Owing to the nature of a prism spectrum, it was difficult for Schumann to determine accurately the wave lengths of the lines which he discovered. Since his paper no attempt seems to have been made to measure these lines. It was in an effort to measure these wave lengths that the false spectra above referred to were first observed.

It seemed probable that if a concave grating could be used to obtain these ultra-violet lines, an accurate determination of their wave length

would be possible. Accordingly, some two years ago, Mr. E. H. Colpitts and the writer undertook the investigation. The methods used and the results obtained were briefly as follows: —

The concave diffraction grating, slit, and photographic plate were all enclosed in an air-tight cast-iron box. Light was admitted to the box through a fluorite window. The source of light was a powerful electric spark, obtained from a transformer run from the commercial circuit; a capacity equivalent to four large Leyden jars was placed in parallel with the spark gap; magnesium was used for terminals. Following Schumann's work, the air was exhausted from the box. The spark was placed close to the fluorite window in order that the column of air between the source and the plate should be as short as possible. Under these circumstances a photograph was obtained showing lines apparently down to wave length 924 μ, a value lower than Schumann's lowest estimated wave length. Terminals of aluminum, cadmium, cobalt, nickel, and copper were tried. All showed lines below 1500 μ; some showed lines as far down as position 950 μ.

During these experiments, the air pressure in the apparatus did not always have the same value. Some plates were taken with the pressure as high as 1 cm.; others with it as low as .2 cm. It was observed that this difference in pressure did not have any effect on the strength of the lines.

Up to this time the first spectrum had been used; now it was desired to find these lines in the second spectrum. In spite of the greatest care, however, no trace of any line below 1900 μ could be found in the second spectrum.

The absence of the lines in the second spectrum, together with their behavior under small differences of air pressure, raised the suspicion that either the lines were not due to light of a very small wave length, or that light of very short wave length was not absorbed by the air to the extent indicated by Schumann. To test this idea the spark was first removed to a metre's distance from the fluorite window. This air column did not reduce the intensity of these new lines. Next, air was admitted to the box, and still the lines were unchanged in intensity, even through a column of air, now five metres long. Evidently the lines were not absorbed by air.

Lest the special brand of plate employed was particularly sensitive to the extreme ultra-violet, a number of different plates were tried. In each case a good photograph was obtained, showing practically all the lines.

A piece of window-glass was placed between the slit and spark, and no

trace of the lines could then be found. Since the light causing these lines is absorbed by glass, and is not absorbed by air, it would seem to have a wave length between 3500 μ and 2000 μ, according to the accepted absorbing power of these two media.

It was now observed that the groups at 2790 μ, 1873 μ, and 924 μ were, even to casual inspection, strikingly characteristic and identical in general appearance. Further, on measuring their dispersions, they were found to be proportional to the displacements of the groups from the slit. Therefore, these groups formed either a remarkable series reproduction or a heretofore unobserved diffraction phenomenon. Thus the issue was definitely raised whether these lines were real first spectrum lines, produced by light of wave lengths 924 μ, 1873 μ, and 2790 μ, and arranged in a 1, 2, 3 series, or whether they were all produced by light of one wave length and owed their position to some diffraction phenomenon connected with the grating.

To distinguish between these alternatives, recourse was had to the relative refrangibility of these lines through quartz. To this end a small angle quartz prism was placed between slit and grating and a short distance from the slit. The effect of this prism was to produce virtual images of the slit whose displacements were nearly proportional to the refrangibility of the light. This device resulted in the displacement of each line in the grating spectra by an amount proportional to the refrangibility of the light producing that line.

If the lines at 1873 μ and 924 μ were caused by light of the same wave length, they would suffer equal displacements. If they were caused by light of different wave lengths, they would be displaced by different amounts.

The experiment was tried, and it was found that the groups at 2790 μ, 1873 μ, and 924 μ all suffered about equal displacements. From 2790 μ down to the region of 1873 μ, the displacement of the groups increased as the wave length decreased. There was then a discontinuity in the rate of increase of the displacement before 1873 μ and a second discontinuity between 1873 μ and 924 μ.

The most obvious conclusion from these data is that the lines at 1873 μ and 924 μ are not due to light of wave lengths corresponding to the positions of the lines in the spectrum. They seem to be caused by light having a wave length near 2800 μ; they seem to be reproductions of some part of the true spectrum, — curious phantom lines due to some property or imperfection of the grating. An examination of the lines below 1900 μ taken with aluminum terminals fully carried out this

theory. Before leaving this first grating, which we will call No. 1, it is important to note that although the groups in magnesium at 2790 μ, 1873 μ, and 924 μ closely resemble each other, their wave lengths are not exactly in the 1 : 2 : 3 ratio; $2 \times 924 = 1848$, which differs from 1873 by 25.

It was proved that these phantom lines were not due to any local variation in ruling by shielding all but a narrow strip of grating surface, and then moving the screen so as to expose each strip in turn. In this way a series of photographs were obtained, each from a different strip of grating surface. They all showed the phantom lines with about equal intensity.

In addition to the grating with which the investigation was begun, three others were examined. Two of these were of larger radius, — 21 ft.; the other was similar in type to the first instrument. Of the two large gratings, one showed the phantom lines distinctly. The two strong groups formerly at 1873 μ and 924 μ were now found at positions corresponding to 1728 μ and 1079 μ. The other large grating did not show the lines at all. The last small grating showed the reproduction of group 2790 μ at positions of about 1870 μ and 924 μ. In addition, however, there were also numerous less distinct reproductions scattered between these two positions.

We may now sum up the facts arrived at in these few pages. Of four concave diffraction gratings examined in this investigation, three showed the phenomenon of phantom lines. These lines vary in position with the grating by which they are produced, but the variation cannot be connected either with the variation of radius of curvature of the grating or with the number of lines to the inch. The most prominent of these phantom lines closely resemble some group in the true spectrum. This repetition of a true group occurs most strongly twice. The width of these phantom repetitions is proportional to their apparent wave length. The wave lengths of the true group and its phantom repetitions bear no simple relation to one another. The photographs obtained with gratings 1 and 4 show a very large number of faint repetitions of a group or set of groups. These repetitions form a sort of background to the main spectrum between 1800 μ and 900 μ.

It may be safely said that a strong line in the spectrum is repeated a great number of times, and that these phantoms are distributed apparently at random. We have no reason to believe that this repetition is confined to a certain proportion of the ultra-violet spectrum. Every line in the spectrum is probably reproduced. These reproductions are con-

cealed by the strong real lines of the spectrum in places where strong lines occur. They are chiefly noticeable in the extreme ultra-violet, where there are no real lines. In parts of the spectrum where gaps occur, however, these phantoms may be visible and may there be mistaken for real lines. Such, in brief, are the results arrived at. A more detailed account of the apparatus and of the numerical results of the investigation will now be given. The consideration of the causes which produce these phantom lines is left for the end of the paper.

FIGURE 1.

The first grating investigated was one of 180 cm. radius. The plate was prepared by Brashear and ruled by Rowland's engine in the year 1897; it had 14,438 lines to the inch. To economize space a mounting somewhat different from that of Rowland was used. The grating and slit were fixed in position at a distance apart equal to the radius of curvature of the grating. The plate-holder was carried by an arm pivoted at a point on the line connecting slit and grating and midway between the two. The length of the arm was, of course, half the radius of the grating. The plane of the grating was so adjusted that the principal image fell about 1 cm. to the right of the slit. This was done to avoid reflection from the polished jaws of the slit. The plate-holder was constructed to take a plate five inches long and one inch broad. The form of the box in which the apparatus was enclosed is not material to this investigation. The spark which served as a source of light was placed within 3 mm. of the fluorite window. In the first experiments the width of the slit was about .1 mm., and the time of exposure was about one hour. Later, however, good photographs were obtained with exposures of from twelve to fifteen minutes. In making tests for the absorption of the air a quartz lens was placed between the source and the slit.

In developing photographs of this type, great contrast is the chief object. The kind of developer used thus becomes important. After several trials, an Ortol-Soda developer was found to give the best results.

The apparent wave lengths of the different lines which come under consideration were determined by comparison with the normal sun spec-

trum. A dividing engine with a $\frac{1}{2}$ mm. screw was used. This screw, when used to measure lines on a six-foot grating possesses for a run of 20 cm. an accuracy better than one one-hundredth of an Ångström unit. The plate was observed by means of a stationary microscope fitted with a four-inch objective and micrometer eye-piece. The value of one centimeter of plate length in terms of Ångström units was determined by measurements taken between two given sun lines, located by Rowland's map. In order to get a photograph of the sun spectrum and the magnesium spectrum on the same plate, a shutter was placed before the slit and so adjusted that the upper or lower half could be exposed at pleasure. By this means two narrow spectra were obtained, one above the other. The method is preferable, when working with the first spectrum, to the usual mode of protecting the plate itself by a swinging screen.

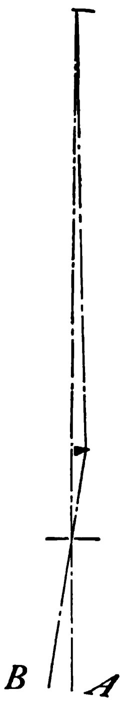


FIGURE 2.

When it became necessary to test the nature of the light producing the lines at 1873 μ and 924 μ in the magnesium spectrum, the following arrangement was adopted: The quartz prism of an angle of five degrees was placed some 30 cm. distant from the slit, but not on the straight line joining slit and grating. Thus when the source was in position A, the light did not fall upon the prism; but when it was in position B, the light passed through the prism. In the first case, the upper half of the slit was closed by the shutter; in the second, the lower half was closed. The result was, of course, to produce two spectra, one above the other; the one due to light which had passed through the prism was thus shifted toward the red. The general appearance may be seen from Plate No. I.

It now becomes necessary to consider more in detail the behavior of the light of these ultra-violet spectra when passed through the quartz prism. The results for magnesium may be seen from the following table. The lettering of the groups on the plans of the spectra is, of course, arbitrary. The chief or real groups are marked with an unsubscripted letter. The reproductions are marked with letters bearing a subscript. The plates are from drawings made from the original photographs. Beginning with magnesium Plate II., six principal groups of lines are to be noted; they extend from the pair of lines marked A_1, — wave length 1966 μ, — to the strong group C_4, — wave length 924 μ. Besides these strong lines, there are six fainter groups

distinctly visible, — A_2, b_1, C_2, A_3, b_2, and C_3. A_2 resembles group A_1, C_2 group C_1; C_3 resembles group C_4, A_3 group A_4. It is to be noted that while A_2 and C_2 lie on the right or ultra-violet side of A_1 and C_1, C_3 and A_3 lie on the left or red side of C_4 and A_4. In addition to the simple groups of lines already mentioned, the whole spectrum, from one end to the other between A_1 and C_4, is filled with a number of fine, faint lines. These lines are not regularly arranged so as to produce fluting, but rather present the appearance of a reproduction of groups of lines.

MAGNESIUM.

Group.	Apparent wave length.	Displacement.
C	2790 μ	42.2 mm.
I	2713 μ	43.4 mm.
II	2682 μ	43.9 mm.
A_1	1966 μ	42.1 mm.
A_2	1924 μ	
b_1	1914 μ	
C_1	1873 μ	42.2 mm.
C_2	1834 μ	42.3 mm.
D_2	1475 μ	39.8 mm.
E_2	1266 μ	40.2 mm.
A_4	969 μ	41.9 mm.
C_3	964 μ	
b_2	944 μ	
C_4	924 μ	42 2 mm.

ALUMINUM.

Group.	Apparent wave length.	Displacement.
I	2376 μ	38.8 mm.
B_1	2075 μ	36.1 mm.
C_1	1890 μ	36.7 mm.
D_2	1300 μ	34.9 mm.
E_2	1184 μ	35.3 mm.
B_3	1023 μ	36.0 mm.
C_3	933 μ	36.6 mm.

If we examine the displacements produced in these groups when the light is allowed to pass through the quartz prism before falling upon the grating, the following facts become evident: A steady increase in displacement is observed in the successive lines going from the strong group at 2790 (C) towards the ultra-violet until we get in the neighborhood of group A_1. At this point the amount of displacement suddenly returns to about the value it had at 2790 μ. Between groups A_1 and D_2 the dis-

placement suffers a second discontinuity. Thus A_1 gives 42.1 mm., D_3 39.8 mm. The displacement of C_4 is almost exactly that of C_1, and very nearly that of group C, — 2790 μ. The figures are 42.25 mm., 42.25 mm., 42.21 mm. As stated before, the most obvious conclusion from these data is that the lines A_1 to C_4 are not due to light of wave lengths corresponding to the positions of the lines in the spectrum. They seem to be reproductions of some part of the true spectrum.

On the aluminum plate there are present six strong lines, — B_1, C_1, D_2, E_2, B_3, C_3, — with wave lengths from 2075 μ to 933 μ. There are faint reproductions of these groups similar in arrangement to those observed with magnesium. There is a background of fine, indistinct lines. On allowing the groups to be displaced by the prism, we find group D_2 less displaced than group C_1, and group B_1 less displaced than a real group called I.

We may now consider the false nature of the lines as established. It remains to investigate the causes which produce this diffraction phenomenon.

It is perfectly evident that the phantoms are not due to a local variation in the rate of ruling, such as produce ghosts; for we have seen that the fault is not local in the grating surface. Moreover, we know that a ghost always occurs close to the line of which it is a reproduction.

The phantoms are not due to a false source of light, since the dispersion of the various reproductions is not the same as that of the real group. We may discard the hypothesis that the mounting of the grating or the position of the source of light has any effect. The lines occur with various forms of mounting and with various positions of lens and source, as will be seen later. We have to deal with a diffraction phenomenon, with an inherent property of the diffraction grating itself.

It seems probable that in developing the theory of the grating some assumptions have been made which are not according to fact. It is in the error of such assumptions that we find the solution of our problem.

It is generally assumed in treating the grating that the lines of the ruling are of equal width and are separated by equal spaces. In the very nature of things, it is evident that this cannot be the case in view of the very minute distances involved and the almost inconceivable rigidity which would be necessary. These variations, slight in absolute amount, may be a considerable fraction of the distance from line to line. It is clear, moreover, on experimental as well as on theoretical ground, that these variations are not local, but extend over the whole surface of the grating.

It appears, then, that the departure from equal spacing assumed in the theory of the concave grating is not the random departure which is next in theoretical simplicity, but a more or less systematic departure which has emphasized disproportionately certain of the subordinate maxima called for in the conventional theory. If the position of the false maxima occurred in the ratio 1 : 2 : 3, or in any other simple ratio, the phenomena would invite an analytic discussion. As an experimental fact, however, our lines are not harmoniously placed with respect to the slit, nor are they arranged according to any discoverable system. Moreover, they are different in character and position when obtained by different gratings ruled by the same engine. It seems most likely that the phantom lines are due to a number of superposed first spectra of varying dispersions; and that these false spectra owe their existence in some manner to the variation in width and separation of the grating lines. Under these conditions, an analytic discussion seems less profitable than the presentation of the experimental data.

In order to substantiate the statements just made, it becomes the next object of the investigation to observe carefully the relative positions of the phantom lines, not only in one, but in several different gratings.

We must observe, in looking over the tables already given, that although several groups bear a strong resemblance to each other, and though the apparent wave lengths of these groups are nearly in one, two, three ratio, this ratio is never exact.

In aluminum, the line C_3 seems to resemble the line C_1, but $2 \times 933 = 1866$, not 1890. The group B_3 resembles B_1, but $2B_3 = 2046$, not 2075. There certainly is no exact 1, 2, 3 relation, although lines corresponding roughly to $3C_3$ and $3B_3$ in wave length may be found for aluminum. The difference between 2046 and 2075 = 29 Ångström units cannot possibly be due to the error of observation. It is perfectly safe to say that the measurements of wave lengths in the table are correct to 1 Ångström unit.

Before examining another grating, there are one or two more points which need attention. A concave grating produces two spectra of the first order, which in this form of mounting lie on each side of the slit. The spectrum on the left had been investigated; it was now necessary to observe the spectrum on the right of the slit. The grating was therefore turned upside down, by which process the spectrum formerly on the right of the slit now fell upon the left. Photographs taken showed the lines A_1, C_1, A_4, C_4, etc., in magnesium as clearly as before. The grat-

ing was next turned about a vertical axis until the direct image of the slit fell upon the plate. No lines below group C_4 were revealed by this process, nor was the position of the lines greatly changed. It must be noted, however, that the turning of the grating will somewhat distort the spectra and change the value of μ to cm.

The second grating to be investigated was of 21 ft. radius, 14,438 lines to the inch. It was arranged on Rowland's mounting. The intensity of the spectra given by this grating was very inferior to that obtained with the 6 ft. instrument. The first spectrum was selected to work with, the magnesium spark was used as a source. It was found necessary to give an exposure of an hour, and to use a slit .2 mm. in width. A good deal of care was taken to have the exposure of the proper length; if too short, the lines themselves would not appear; if too long, the lines would be obscured by fog. With this 21 ft. grating, a very little fog would quite shield any very faint line. After some trouble, the characteristic reproductions of group 2790 were found. They now occurred, however, at positions corresponding to wave lengths of 1728 μ, 1079 μ. The widths of the groups were 4.8 mm., 2.8 mm., 1.8 mm. Thus, though these phantom lines have different apparent wave lengths when measured on different gratings, their dispersion seemed proportional to their wave length. It must be noted that with grating No. 2 only the lines called A_1, C_1, and A_4, C_4 are visible, the other fainter lines, as well as the fluted effect in the background, being totally absent. This is well accounted for by the feebleness of the spectrum obtained from grating No. 2. The apparent wave length of these groups was obtained by the same method as that previously employed. Owing to the great distance between the head group (2790) C and its reproductions, a cathetometer was used. The results are correct, however, to better than 2 Ångström units. The widths of the groups were measured on the dividing engine and are correct to within .03 mm. The value of 1 cm. of plate length was obtained from measurements between two sun lines.

I feel certain that groups 2790 μ, C_1 and C_4 as obtained with grating No. 2 are not in 1 : 2 : 3 ratio.

The next grating investigated was one of 21,000 lines to the inch and 21 ft. radius. Here the illumination was even more feeble than with grating No. 2. Great trouble was experienced from fog. The lines in magnesium, C_1 and C_4, could not be found. The last grating examined was similar to No. 1. It had a radius of 183 cm., 14,438 lines to the inch; it was prepared by Brashear; it was ruled by Rowland's engine at

Johns Hopkins in the year 1894. The mounting was the same as that of grating No. 1.

The character of the photographs obtained with grating No. 4 was quite different from those obtained with grating No. 1. Lines A_1, C_1, and A_4, C_4 were present, and with about the same apparent wave length as before. They were, however, very much less distinct than when obtained with grating No. 1. The fluting effect was not very sharp; but, on the other hand, the space between positions $1878\,\mu$ and $924\,\mu$ was filled with reproductions of groups A_1 and C_1, of such clearness as to be quite unmistakable. The wave lengths of some of these phantom lines was determined in the same manner as before. Groups corresponding in appearance to the family marked A_1, A_2, A_3, etc., were found at $1970\,\mu$, $1020\,\mu$, $993\,\mu$, and $970\,\mu$. The groups called C_1, C_2, etc., were found at $1878\,\mu$ and $924\,\mu$ very clearly, and at more than eight other positions in a less distinct form between 1878 and 924. In fact, the spectrum in this region is so filled with groups of the A, C, type that the lines of one family overlap lines of the other in many cases.

Such, then, are the experimental data connected with this phenomenon. Before coming to a statement of conclusions, however, the following facts are of interest: —

Some of the reproductions belonging to the set of lines A_2 and E_2 in aluminum occur under the real spectrum, and may be observed if proper care is used.

Gratings of large radius do not show the false lines with as much clearness as gratings of small radius. So feeble, indeed, are the false lines obtained with the 21 ft. grating, that it is improbable that they would be noticeable in ordinary spectrum work. With a six-foot grating, however, the false lines are so strong that they might easily cause errors in series spectrum investigations. We have seen, moreover, that the false lines from grating No. 1 are much stronger than those from grating No. 4, and we have reason to suspect that gratings exist which produce false lines even stronger in character than those obtained with grating No. 1. Gratings 1 and 4 differ little in radius, and have exactly the same number of lines to the inch, yet their false spectra are entirely different in character. We cannot apparently predict the nature of the false spectra of one grating from the false spectra produced by another of the same ruling and radius.

The conclusions arrived at in this paper may be stated as follows: —

1. The first spectrum produced from the Rowland concave grating is not pure, but is complicated not only by underlying spectra of

higher order, but by the presence of a number of spectra of lower dispersion.

2. The number and dispersion of these false spectra obey no simple law, but present the appearance of a reproduction of some real group or groups distributed at random.

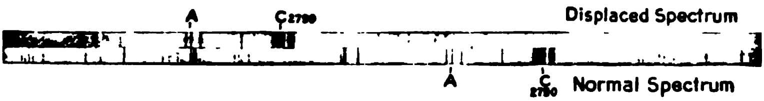
3. The number, dispersion, and clearness of these spectra differ with different gratings.

4. The lines due to the false spectra are most clearly visible in the extreme ultra-violet, owing to the absence of strong real lines, and are so pronounced as to screen any feeble real line that may occur in this region.

Jefferson Physical Laboratory, Harvard University,
Cambridge, Mass., October, 1900.

Lyman. — False Spectra.

PLATE I.

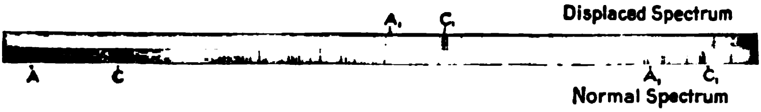


MAGNESIUM

PLATE II.

MAGNESIUM

PLATE III.



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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CASE SCHOOL OF APPLIED SCIENCE.

INVESTIGATIONS ON THE COMPOSITION OF PETROLEUM.

By Charles F. Mabery.

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INVESTIGATIONS ON THE COMPOSITION OF PETROLEUM.

By Charles F. Mabery.

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No. 85. — ON THE COMPOSITION OF CALIFORNIA PETROLEUM.

By Charles F. Mabery and Edward J. Hudson.

In its composition as a natural product, California petroleum is the most interesting of any of the numerous petroleums that have come under our observation. When its constituents are more fully understood they will doubtless shed new light on the origin of petroleum, from the fact that they have been subjected to less rigorous agencies during, or subsequent to, their formation than petroleums from other well-known fields. In fields not yet developed, such as those of South America and Japan, similar unstable oils are found. It is useless to attempt to separate from these peculiar oils their individual constituents by the ordinary method of fractional distillation under atmospheric pressure. Not only on account of the high boiling points, but because the presence of air causes such decomposition, hydrocarbons boiling above 200° cannot be separated in a pure form without the aid of a vacuum. With no further knowledge of the constituents of the crude oils, this explains the numerous ineffectual attempts during the last thirty years to obtain acceptable refined products from California petroleum. By excluding air, as in vacuum distillation, with the reduction of boiling points, it is possible to distil without decomposition all the hydrocarbons of the crude oils. With some modifications of the apparatus employed in vacuum distillation of the higher fractions of Pennsylvania oil, the fractional separation may be carried on with little more delay than in distillation under atmospheric pressure.

Provision for drawing in fresh fractions without loss of vacuum may be made by sealing on a second tube to the neck of the flask a little lower than the exit tube for the escaping vapors. Then, as in the ordinary application of the Hempel principle, the cooling space in the neck of the flask may be increased by filling it with broken glass. This requires a long-necked flask, and the beads may be supported on a piece of glass rod resting on the bottom of the flask, the upper end flattened so as nearly to fill the neck of the flask as a support to the broken glass. The chief hindrance to the use of beads is the condensation of liquids with high boiling points in the neck of the flask, due to the cooling effect of the outside air. The neck of the flask must, therefore, be packed an inch or more thick with asbestos. With this arrangement, and with a flat perforated ring burner for heating, the distillation may be conducted with a fairly rapid fractional separation, without decomposition even of the constituents that distil above 350°, 50 mm.

This examination of California oil was undertaken with the intention of ascertaining the series of hydrocarbons which constitute the main body of the crude oil, as well as the principal members of the series, as shown by percentage composition and molecular weights.

The first specimen of crude oil was received through the kindness of Mr. C. A. Black, chemist in an oil company in Ventura County. The second specimen came from a well of the Coalinga Oil Company in Fresno, through the secretary of the company, Mr. Henderson Hayward. These two specimens will be referred to respectively as Ventura oil and Fresno oil. Another specimen was received from the Puente Hills in Los Angeles County, through the kindness of the Puente Oil Company at Chino. This oil will be referred to as Puente oil. Four other specimens were received from the Torrey wells and the "Los Angeles" wells in the Sespe district (Scott's Hill) in Ventura County, through the kindness of the Union Oil Company at Santa Paula. These samples will be designated respectively as Adams' Cañon, Bardsdale, Scott's Hill, and Torrey oils.

Another specimen is of especial interest, since it came from a well sunk beneath the Pacific Ocean at high tide. It was sent by Mr. J. B. Treadwell from a well at Summerland, Santa Barbara County, at a point where the oil strata outcropped on a north and south line at the top of an elevation, and again descending on the south side, disappeared under the ocean. The well was driven to a depth of 245 feet, just within the shore line at high tide, where it reached the bottom of the oil sand. This oil will be referred to as Santa Barbara oil.

This collection of specimens seemed to offer a fair average of the oils from the California fields, representing four different counties, and deposits that yield oil in considerable quantities.

Since these crude oils differed essentially in their appearance and in their physical properties, in ascertaining their composition it seemed advisable to examine them individually.

In the spring of 1897 an examination of the Ventura oil was begun,* and besides giving the composition of the crude oil, the fractional separations were carried far enough *in vacuo* to identify the principal constituents boiling below 175°. The several hydrocarbons homologous with benzol, which have been found in petroleum from other sources, were found to constitute a large part of the unpurified distillates; but the chief constituents were shown by their composition and specific gravity to be methylenes, for the first time recognized as essential constituents of American petroleum.

Petroleum from Fresno County.

A brief account of the composition of a specimen of crude oil from Fresno County was given in the preliminary paper referred to above. When this oil was subjected to distillation, it was evident that decomposition could only be prevented in the fractions above 150° by collecting them *in vacuo*. The portion collected below 150° atmospheric pressure — 2090 grms. — was submitted to long continued fractional separation within 1° until 50 grms. collected below 55°, and only 5 grms. between 55° and 68°. At 68°–70° the distillates amounted to 60 grms., which was separated for the most part at 68°. The specific gravity of the crude distillate at 68° was found to be 0.6913, and after thorough agitation with fuming sulphuric acid, 0.6844. A combustion of the purified oil gave the following percentages of carbon and hydrogen: —

0.1692 grm. of the oil gave 0.5234 grm. CO_2 and 0.2314 grm. H_2O.

	Calculated for		Found.
	C_8H_{16}.	C_8H_{18}.	
C	85.70	83.72	84.38
H	14.30	16.28	15.30

The loss in this analysis is doubtless due to an escape of a very small amount of gaseous decomposition products without complete combustion. Combustion of such a volatile oil requires the closest attention in manip-

* Am. Chem. Journ., XIX. 796 (1897).

ulation to avoid loss in transferring to the combustion tube, and as will appear later, the highest temperature that the hardest tube will stand is necessary for complete combustion. These results seem to indicate that the oil was a mixture of hexane and hexamethylene. The slight change in specific gravity after treatment with fuming sulphuric acid and potassic hydrate shows that the benzol had been almost completely removed. The fractions at 68° appear to be the last in California oil containing members of the series C_nH_{2n+2}. Since small quantities of distillates collected in the vicinity of 60°, 38°, and in one specimen at 30°, it is probable that the very light gasoline from California oil has the same composition as that from Pennsylvania oil.

The specific gravity of hexane, 0.6630 at 18°, and of hexamethylene, 0.690, also indicate that the fraction 68°–70° is a mixture of these two hydrocarbons.

Heptamethylene, C_7H_{14}.

The distillate collected at 96°–98° amounted to fifty grams. Before purification it gave as its specific gravity 0.7499, and after purification, 0.7413. The specific gravity of heptane boiling at this point is 0.6440 (20°.5). Beilstein and Kurbatoff gave 0.742 at 18° as the specific gravity of heptanaphtene. A combustion gave the following percentages of carbon and hydrogen: —

0.1413 grm. of the purified oil gave 0.4442 grm. CO_2 and 0.1814 grm. H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.70	85.74
H	14.30	14.35

A determination of the vapor density of the fraction 96°–98° by collecting the vapor over mercury gave a value corresponding to the molecular weight of heptamethylene. The determination was made by the method of V. Meyer, *in vacuo*, essentially according to the modification of Lunge and Neuberg: *—

0.0494 grm. of the oil gave 22.9 c.c. under a tension of 373 mm. and at 24°.

Calculated for C_7H_{14}.	Found.
3.40	3.40

* Ber. deutsch. Gesell., 1891, 729.

The high specific gravity of this hydrocarbon corresponding to that of heptanaphtene, the composition given by analysis and the molecular weight, leave no doubt that this body is a heptamethylene, and that heptane is not contained in California (Fresno County) petroleum.

Benzol.

The distillates in the vicinity of 80°, especially 79°–81°, gave the characteristic odor of benzol. 20.5 grms. of these fractions shaken below 60° with a mixture of nitric and sulphuric acids, gave a heavy nitro-product; after washing with water and distilling, the distillate weighed 13 grms., showing that 35.5 per cent of this oil was benzol. Some of the same fractions treated with fuming nitric acid deposited needle-shaped crystals that melted at 89°–90°, the melting point of dinitrobenzol.

Toluol.

After the twelfth distillation, 60 grms. collected at 109°–110° with the penetrating odor of toluol. 30 grms. of this distillate was shaken with a mixture of nitric and sulphuric acids, and the oil not nitrated separated from the nitro-product by distillation. The distillate weighed 13 grms., showing that 54 per cent of the original distillate was toluol. Upon agitating this product with fuming sulphuric acid and distilling, 1.6 per cent more was removed. The remaining oil was dried over sodium for analysis.

The unpurified distillate gave the following values on analysis: —

0.1584 grm. of the oil gave 0.5090 grm. CO_2 and 0.1663 grm. H_2O.

	Calculated for Toluol.	Calculated for C_nH_{2n}.	Found.
C	91.31	85.70	87.64
H	8.69	14.30	11.73

The change in composition by treatment with acids was very marked: —

0.1725 grm. of the purified oil gave 0.5387 grm. CO_2 and 0.2282 grm. H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.70	85.20
H	14.30	14.71

Evidently the small quantity of oil remaining after the treatment with acids was octonaphtene, that had not been completely separated by distillation.

Octonaphtene, C_8H_{16}.

After the twentieth distillation, 30 grms. collected at 118°–120°, which, with no further purification than drying over sodium, gave 0.7615 as its specific gravity at 20°, and, on analysis, values required for octonaphtene: —

0.1457 grm. of the oil gave 0.4566 grm. CO_2 and 0.1922 grm. H_2O.

C	85.47
H	14.71

After thorough treatment with fuming sulphuric acid the specific gravity was reduced to 0.7532, at 20° (octonaphtene, 0.7582 at 17°.5, Beilstein and Kurbatoff), but the composition was scarcely changed: —

I. 0.1471 grm. of the oil gave 0.4618 grm. CO_2 and 0.1895 grm. H_2O.
II. 0.1334 grm. of the oil gave 0.4185 grm. CO_2 and 0.1762 grm. H_2O.

	Calculated for C_nH_{2n}.	Found. I.	II.
C	85.70	85.62	85.54
H	14.30	14.32	14.67

After the eighteenth distillation, 25 grms. remained persistently at 124°–125°, which was not affected by fuming sulphuric acid in the cold, but at 100° the acid became colored and gave off much SO_2. On pouring into water, the solution gave a peculiar odor resembling turpentine, and a black powder separated that contained nitrogen. Analysis of the distillate after the treatment with the acid gave values required for C_nH_{2n}: —

0.1391 grm. of the oil gave 0.4354 grm. CO_2 and 0.1875 grm. H_2O.

	Required for C_nH_{2n}.	Found.
C	85.70	85.36
H	14.30	14.98

Since no other hydrocarbon than normal octane has been recognized with this boiling point, this distillate must be a mixture of octonaphtene with a higher body, but evidently normal octane is not present in appreciable quantity.

Nononaphtene, C_9H_{18}.

A considerable quantity of distillate collected at 134°–135°, that gave as its specific gravity 0.8175. After purification with fuming sulphuric

acid its specific gravity was reduced 0.7591. 28 grms. of the crude distillate gave 13 grms. of the purified oil with a loss of 53 per cent. The purified oil gave by the action of fuming nitric acid a nitro-derivative that, after crystallization from glacial acetic acid, melted at 85°. The melting point of dinitromesitylene is 86°. A combustion of the purified distillate gave values for carbon and hydrogen required for nononaphtene: —

0.1382 grm. of the oil gave 0.4318 grm. CO_2 and 0.1827 grm. H_2O.

	Calculated for C_9H_{18}.	Found.
C	85.70	85.21
H	14.30	14.68

Xylols.

Since para- and meta- xylols have frequently been found in petroleum, it did not seem advisable to separate the isomeric xylols, although the distillates 137°–140° gave the strong penetrating odor of these bodies. At the end of the thirteenth distillation, 630 grms. collected within these limits. On treating 125 grms. of this product with a mixture of nitric and sulphuric acids, and agitating below 60°, washing with sodic hydrate and water, drying and distilling, only 50 grms. came over below 145°, showing that the xylols formed 60 per cent of the original distillates and had been removed as nitro-products. At the low temperature of the nitration only the aromatic hydrocarbons could have been affected. The change in composition by the nitration is shown by the following analyses: —

0.1469 grm. of the unpurified oil gave 0.4770 grm. CO_2 and 0.1495 grm. H_2O.

	Calculated for Xylol.	Found.
C	92.31	88.53
H	7.69	11.31

Analysis of the purified distillate gave the following results on analysis: —

I. 0.1382 grm. of the oil gave 0.4318 grm. CO_2 and 0.1827 grm. H_2O.

II. 0.1386 grm. of the oil gave 0.4318 grm. CO_2 and 0.1837 grm. H_2O.

III. 0.1441 grm. of the oil gave 0.4492 grm. CO_2 and 0.1901 grm. H_2O.

	I.	II.	III.	C_nH_{2n}.
C	85.21	84.96	85.00	85.70
H	14.69	14.72	14.66	14.30

The chief portion of the nitrated oil was shown to be meta xylol, since the nitro-compound distilled at 240°–260°, and with fuming nitric acid it was converted into a crystalline powder insoluble in alcohol; crystallized from glacial acetic acid, it melted at 176°, the melting point of trinitrometaxylol. Probably the fifty grams not nitrated was for the most part nononaphtene.

Nonane.

Since considerable quantities of distillates collected in the vicinity of 150°, after the seventeenth distillation, attempts were made to ascertain whether nonane is a constituent of California petroleum. This seemed of especial importance since nonane forms such an important constituent of Pennsylvania petroleum. Without purification a combustion showed the following proportions of carbon and hydrogen: carbon, 86.14; hydrogen, 12.67. The specific gravity was 0.8117. After agitating several times with fuming sulphuric acid, the composition was materially changed: —

0.1719 of the oil gave 0.5372 grm. CO_2 and 0.2206 grm. H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.70	85.20
H	14.30	14.26

The principal constituent of this fraction was therefore a naphtene or a mixture of naphtenes.

Dekanaphtene, $C_{10}H_{20}$.

At the end of the seventeenth distillation, the quantity of distillates within one degree limits between 159° and 163° amounted to 150 grms. By further distillation these came together for the most part at 160°–161°. The specific gravity of the unpurified distillate at 20° was 0.8272. When agitated in the cold with fuming sulphuric acid, this distillate developed great heat; after treatment several times, until the acid was no longer much colored, the product was washed with sodic hydrate and water and dried for analysis. The original distillate lost 75 per cent of its weight by this treatment. The aromatic hydrocarbon

doubtless consisted, for the most part at least, of ethyl toluol, boiling point 161°–162°, but no further attempts were made to identify it.

The specific gravity of the residual oil was 0.7841, practically the same as the specific gravity of dekanaphtene, 0.783, separated by Markownikoff and Oglobine from Baku petroleum. Its odor is precisely similar to that of the corresponding hydrocarbon which one of us (Mabery) has separated from crude Baku oil.

Analysis of the unpurified distillate gave the following values: —

I. 0.1462 grm. of the oil gave 0.4724 grm. CO_2 and 0.1524 grm. H_2O.
II. 0.1496 grm. of the oil gave 0.4844 grm. CO_2 and 0.1564 grm. H_2O.

		Found.
C	88.10	88.28
H	11.57	11.61

After treatment with the acid the composition was materially changed; the results correspond closely to the composition of dekanaphtene: —

0.1481 grm. of the oil gave 0.4646 grm. CO_2 and 0.1932 grm. H_2O.

	Calculated for $C_{10}H_{20}$.	Found.
C	85.70	85.55
H	14.30	14.50

A determination of the molecular weight gave a value required for dekanaphtene.

0.8850 grm. of the oil and 24.22 grms. benzol gave, by the Beckman method, at the freezing point, a depression of 1°.28.

Calculated for $C_{10}H_{20}$.	Found.
140	140

After the twenty-fourth distillation, 50 grms. collected at 169°–170°, which gave as its specific gravity without purification, 0.8358. After thorough agitation with fuming sulphuric acid and washing, the specific gravity was reduced to 0.7749, but the larger portion of the oil was removed by the acid, indicating that the fraction consisted for the most of a benzol homologue. The small quantity remaining after the treatment was doubtless dekanaphtene, since its specific gravity was nearly the same.

The presence of a naphtene in Russian oil, boiling at 182°, led us to believe that the same body should be found in California oil. But

the small quantity of distillate collecting here, only 10 grms. after long distillation, excluded this hydrocarbon in any appreciable quantity.

UNDEKANAPHTENE, $C_{11}H_{22}$, 195°.

Between 188° and 191°, 50 grms. came together at the end of the tenth distillation, which gave the following results on analysis: —

0.1423 grm. of the oil gave 0.4550 grm. CO_2 and 0.1617 grm. H_2O.

	Calculated for $C_{11}H_{22}$.	Found.
C	85.70	87.20
H	14.30	12.63

The specific gravity of this distillate before treatment was 0.8386. After vigorous agitation with fuming sulphuric acid, and washing, the specific gravity was reduced to 0.8044.

A distillate separated from Russian oil at 197° gave (Markownikoff and Oglobine) as its specific gravity at 14°, 0.8055, and it was assigned the formula $C_{12}H_{24}$. The quantity of oil remaining after separation of durol, which no doubt was the benzol hydrocarbon in this distillate, was small. That it was a naphtene, as shown by its specific gravity, is confirmed by analysis: —

0.1459 grm. of the oil gave 0.4575 grm. CO_2 and 0.1886 grm. H_2O.

	Calculated for $C_{12}H_{24}$.	Found.
C	85.70	85.70
H	14.30	14.40

Determinations of the molecular weight of this fraction by the Beckman freezing point method using benzol gave the following value: —

0.7901 grm. of the oil and 24.68 grms. benzol gave a depression of 1.°012.

1.1249 grm. of the oil and 25.90 grms. benzol gave a depression of 1°.36.

Calculated for $C_{11}H_{22}$.	Found. I.	Found. II.
154	155	157

It appears from these results that the hydrocarbon in California petroleum boiling at 195° is not dodekanaphtene, $C_{12}H_{24}$, but undekanaphtene, $C_{11}H_{22}$. This conclusion is further confirmed, as will appear later, by the composition of the distillate 216°, which appears to be dodekanaphtene,

and still further by the composition of the monochlornaphtene obtained from the hydrocarbon boiling at 195°, which gives as its formula $C_{11}H_{21}Cl$.

In the vicinity of 200°, 50 grms. of a distillate collected which gave as its specific gravity 0.8684. After agitation with fuming sulphuric acid, the specific gravity was diminished to 0.8202. An analysis before treatment gave 87.84 per cent of carbon and 11.91 per cent of hydrogen. After treatment with the acid, the analysis gave 85.99 per cent of carbon and 13.97 per cent of hydrogen, showing that some of the aromatic hydrocarbon still remained; the small amount of naphtene was doubtless undekanaphtene, boiling at 195°; specific gravity, 0.8010, as given above.

Dodekanaphtene, $C_{12}H_{24}$.

A considerable quantity of distillate collected at 208°–210°, corresponding to 216°, which corresponded in composition by analysis and molecular weight to dodekanaphtene: —

0.1496 grm. of the oil gave 0.4677 grm. CO_2 and 0.1962 grm. H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.70	85.26
H	14.30	14.57

Determinations of the molecular weight of this product by the Beckman method at the freezing point, gave results corresponding to the formula of dodekanaphtene.

1.0141 grm. of the oil and 25.61 grms. benzol gave a depression of 1.17.

Calculated for $C_{12}H_{24}$.	Found.
166	166

It is therefore evident that California petroleum differs from Russian oil in containing dodekanaphtene, boiling at 216°, as well as undecanaphtene, boiling at 195°.

Puente Oil.

The specimen received from the Puente Oil Company was somewhat thicker than the Fresno oil. Its specific gravity at 20° was found to be 0.892. It contained 0.80 per cent of sulphur. Two determinations of nitrogen by the Kjeldahl method gave, (I.) 0.564, (II.) 0.587; and by the absolute method, measuring the volume of nitrogen, (I.) 1.18, and

(II.) 1.22. A combustion of the crude oil gave, 84.96 per cent of carbon and 11.96 per cent of hydrogen. Two determinations of bromine absorption gave, (I.) 18.8, (II.) 18.3 per cent.

A distillation of 1346 grms. of the crude oil under atmospheric pressure gave the following weights: —

-100°	100°-150°	150°-200°	200°-250°	
167	170	132	130	Grms.

The small proportions distilling below 250° made it evident that the chief constituents could only be separated *in vacuo*. The specific gravity of these distillates at 20° were ascertained by weighing on a Westphal balance: —

100°	100°-150°	150°-206°
0.7642	0.8155	0.8538

Ten litres of the Puente crude oil, after collecting below 150° at atmospheric pressure, gave the following weights under 50 mm: —

150 At. Pr.	-120°	120°-150°	150°-175°	175°-185°	185°-200°	
590	800	827	990	160	495	Grms.

The residue above 200° was next divided into fractions of convenient size without noting temperatures: —

1.	2.	3.	4.	
655	1010	670	430	Grms.

Further distillation of the fraction -150 At. Pressure gave the following weights: —

-60°	60°-62°	66°-68°	78°-82°	88°-90°	96°-98°	109°-110°	118°-120°	
10	10	10	27	40	120	60	65	Grms.

Smaller weights collected at intermediate temperatures.

Heptamethylene, C_7H_{14}.

No attempts were made to ascertain the composition of the individual fractions below 96° from Puente oil. Those portions will receive further attention with the corresponding distillates from the other oils. Without purification the distillate 96°-98° gave as its specific gravity at 20°, 0.7499. After repeated agitation with fuming sulphuric acid and potassic hydrate, the specific gravity was scarcely changed, 0.7440;

specific gravity of heptanaphtene, 0.742 at 18°. Analysis I. was made of the untreated oil, analysis II. of the portion after treatment: —

I. 0.1409 grm. of the oil gave 0.4438 grm. CO_2 and 0.1683 grm. H_2O.
II. 0.1396 grm. of the oil gave 0.4383 grm. CO_2 and 0.1792 grm. H_2O.

	Calculated for C_7H_{14}.	Found. I.	Found. II.
C	85.70	85.90	85.60
H	14.30	13.27	14.26

The difference in analysis I. is doubtless due to oxygen and nitrogen compounds, since agitation of the crude distillates with potassic hydrate separates from most of the distillates from California petroleum heavy oils, with an odor resembling that of creosote. A description of these oxygenated compounds is reserved for a later paper. The specific gravity of the purified fraction, 0.7440, is essentially the same as that of heptanaphtene separated from Russian oil, 0.748, by Beilstein and Kurbatoff.

OCTONAPHTENE, C_8H_{16}.

The fraction 118°–120°, without further treatment, gave as its specific gravity at 20°, 0.7615, which was reduced to 0.7540 by agitation with fuming sulphuric acid. Specific gravity of octonaphtene, 0.7552 at 17°.5. Analysis I. was made of the crude distillate, and analysis II. of the oil after purification with the acid.

I. 0.1406 grm. of the oil gave 0.4424 CO_2 and 0.1760 grm. H_2O.
II. 0.1503 grm. of the oil gave 0.4692 grm. CO_2 and 0.1941 grm. H_2O.

	Calculated for C_8H_{16}.	Found. I.	Found. II.
C	85.70	85.81	85.20
H	14.30	13.91	14.35

No further examination was made of the fractions from 120° to 148°, but it seemed of interest to ascertain whether nonane formed any part of the distillate 148°–150°, since it forms such a large proportion of the Eastern oils. The crude distillate 150°–151° gave as its specific gravity 0.7910, and after purification with sulphuric acid, 0.7730. Analysis of the treated oil gave percentages of carbon and hydrogen that still showed the presence of the benzol homologue.

0.1449 grm. of the oil gave 0.4589 grm. CO_2 and 0.1807 grm. H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.70	86.37
H	14.30	13.57

From the results of this analysis it is evident that nonane forms no appreciable proportion of Puente oil.

Dekanaphtene, $C_{10}H_{20}$.

50 grms. of a distillate collected at 160°–162°, with smaller quantities on either side. A determination of its specific gravity at 20° gave 0.7966, and after agitation with sulphuric acid, 0.7745. The composition of this distillate after treatment with the acid was shown by analysis: —

0.1747 grm. of the oil gave 0.5515 grm. CO_2 and 0.2185 grm. H_2O.

	Calculated for $C_{10}H_{20}$.	Found.
C	85.70	86.09
H	14.30	13.90

Fraction 168°–172°.

In all the California oils examined, as stated above, considerable quantities have collected at 168°–172°. Since large proportions of the benzol hydrocarbons appear in all these oils, the distillate 168°–172° might consist to a large extent of pseudocumol, boiling point 168°. The high specific gravity of the fraction before treatment with the acid, 0.8063, and the lower value after treatment, 0.7874, indicates a considerable proportion of the benzol homologue. Even after the acid treatment, the percentages of carbon and hydrogen showed the presence still of the same constituent: carbon, 85.91; hydrogen, 13.61. It seems probable, therefore, that the benzol homologue constitutes the greater part of this distillate, and the residue after treatment is doubtless higher or lower constituents. But the absence of a decane corresponding to the decane in Pennsylvania petroleum, boiling at 172°, is assured.

Fraction 180°–182°.

Only 10 grms. collected at 180°–182°, with smaller quantities on either side. Although this quantity of the oil was insufficient for complete examination, its specific gravity before and after analysis was ascertained, and an analysis made after treatment with acid. Before treatment the

value obtained was 0.8116, and afterward 0.7955. A combustion gave 86.27 per cent of carbon, and 13.79 per cent of hydrogen. Evidently, like the Fresno oil, Puente oil has no constituent with this boiling point, except perhaps a benzol homologue.

UNDEKANAPHTENE, $C_{11}H_{22}$, 195°.

A naphtene should be expected between 190° and 200°, since undekanaphtene, $C_{11}H_{22}$, is a constituent of the Fresno oil. The 20 grams collecting at 190°–192° gave as its specific gravity at 20°, 0.8196, and after treatment with fuming acid, 0.8046 (0.8055 at 14°, Markownikoff). A combustion of the oil after treatment gave 85.90 per cent of carbon and 13.85 per cent of hydrogen.

The series C_nH_{2n+2} forms no part of the Puente oil, at least above 95°. The low percentage of hydrogen seems to indicate a series still poorer in hydrogen than the naphtenes, especially in the higher distillates, possibly a series C_nH_{2n-2}, containing two naphtene rings. Whether such hydrocarbons are really present, or whether benzol homologues have not been completely removed, will appear in more prolonged distillation of these oils boiling above 200°.

BARDSDALE OIL.

The specimen marked Owens No. 2, sent by the Union Oil Co. from the Bardsdale district, was quite thick and heavy. Its specific gravity at 20° was 0.8923. It contained 1.25 per cent of nitrogen, as shown by the volume of nitrogen collected. A Kjeldahl determination gave 0.50 per cent. A Carius determination gave 1.5 per cent of sulphur, showing it to be a high sulphur oil. A combustion gave 84.17 per cent of carbon and 12.15 per cent of hydrogen. 108 grms. of the oil distilled under atmospheric pressure gave the following weights: —

-150°	150°-310°	310°-410°	
9	24	7	Grms.
0.7433	0.8170		Specific gravity.

In distilling 5088 grms. under 50 mm., except –150° the following weights were obtained: —

-150° At. Pr.	150°-200°	200°-250°	250°-290°	
250	555	374	1165	Grms.

The two fractions below 200° were distilled within 5°, and then within 2°, which brought together the following weights with smaller quantities at neighboring temperatures: —

96°-100°	116°-120°	136°-140°	148°-150°	158°-162°	168°-172°	190°-194°
34	25	35	40	60	20	40 Grms.

The lower portions of this oil began to come over at 45°, but only small quantities collected below 65°. At 65°-70°, 40 grms. collected, which will be examined in connection with the similar distillates from the other oils to ascertain whether the principal constituent is hexane or hexamethylene. The high specific gravity of this oil, even after treating thoroughly with fuming sulphuric acid, 0.7017, would seem to exclude hexane; specific gravity, 0.6671.

Heptamethylene, C_7H_{14}.

The unpurified fraction 96°-100° gave as its specific gravity at 20°, 0.7395, and after treatment with fuming acid, 0.7384. The slight change in specific gravity indicates that this fraction consists for the most part of one hydrocarbon, and analysis with the boiling point shows that the hydrocarbon is heptamethylene; specific gravity, 0.7420: —

0.1473 grm. of the oil gave 0.4620 grm. CO_2 and 0.1879 grm. H_2O.

	Calculated for C_7H_{14}.	Found.
C	85.70	85.54
H	14.30	14.18

Octonaphtene, C_8H_{16}.

The specific gravity of the fraction 116°-120° was 0.7625, and after treatment with fuming sulphuric acid, 0.7566, which indicated that this product contained very little of the benzol homologues. An analysis after purification gave proportions of carbon and hydrogen required for octonaphtene: —

0.1780 grm. of the oil gave 0.5572 grm. CO_2 and 0.2287 grm. H_2O.

	Calculated for C_8H_{16}.	Found.
C	85.70	85.39
H	14.30	14.28

Fraction 150°-152°.

The distillates above 120° received no further attention, except to ascertain that the xylols were present in large proportion, as in the other oils. To ascertain whether nonane is contained in this oil, the specific gravity of the fraction 150°-152° was ascertained and found to be

0.7756, after treatment with the fuming acid. Its composition after treatment with the acid corresponded to that of C_nH_{2n}: —

0.1434 grm. of the oil have 0.4480 grm. CO_2 and 0.1839 grm. H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.70	85.20
H	14.30	14.25

The lower specific gravity of nonane and the results of analysis show that nonane is not a constituent of this oil.

Dekanaphtene, $C_{10}H_{20}$.

The specific gravity of the unpurified fraction 160°–162° at 20° was 0.7966, and after purification with fuming sulphuric acid and sodic hydrate was 0.7905 ($C_{10}H_{20}$, 0.7950 at 0° Markownikoff).

It gave the following results on analysis: —

I. 0.1471 grm. of the oil gave 0.4625 grm. CO_2 and 0.1907 grm. H_2O.
II. 0.1475 grm. of the oil gave 0.4477 grm. CO_2 and 0.1813 grm. H_2O.

	Calculated for $C_{10}H_{20}$.	Found. I.	Found. II.
C	85.70	85.50	85.86
H	14.30	14.37	14.17

On account of the small amount of the distillate 167°–170°, no examination was made of it. It was doubtless chiefly a benzol homologue.

Fraction 176°–178.

To ascertain whether a naphtene boiling at 182° is present in this oil, the fraction 176°–178° was treated thoroughly with fuming sulphuric acid and sodic hydrate. Its specific gravity before treatment was 0.8116; after treatment, 0.7955. It gave on analysis 86.01 per cent carbon and 13.31 per cent hydrogen, indicating still the presence of a benzol homologue. But the small quantity remaining showed the absence of any other constituents with this boiling point in this distillate.

Undekanaphtene, $C_{11}H_{22}$.

The fraction 190°–194° gave 0.8186 as its specific gravity before treatment with fuming sulphuric acid and sodic hydrate, and afterward, 0.8046. Markownikoff found 0.8119 at 0° as the specific gravity of dodekanaphtene from Baku oil.

The percentages of carbon and hydrogen given by analysis supported the formula of undekanaphtene: —

0.1466 grm. of the oil gave 0.4588 grm. CO_2 and 0.1909 grm. H_2O.

	Calculated for $C_{11}H_{22}$.	Found.
C	85.70	85.37
H	14.30	14.47

Some of the Bardsdale distillates, 140°–220°, 50 mm., turned pink soon after they were collected, changing to a darker red on standing, and after some time they deposited a dark oil. The colored distillates alternated with the others, leaving sharply lined uncolored oils beside those depositing the insoluble heavy oils. The following distillates were colored: —

154°–156°, 158°–160°, 168°–170°, 180°–182°, 198°–206°, 212°–216°.

The distillates between these were nearly or quite colorless. This coloration was caused by the phenol bodies, which are easily extracted by alkaline hydrates. The bodies will receive further attention in another paper.

Adams' Cañon Oil.

The Adams' Cañon Oil from the Ex-Mission district was thicker and heavier than the oils previously described. The specific gravity of this specimen at 30° was 0.9212. It contained a large percentage of nitrogen, 1.46, determined by the volume of nitrogen. The Kjeldahl method gave 0.58 per cent. Two determinations of sulphur gave, (I.) 0.92, (II.) 0.87. This oil contained a very small proportion of the lower hydrocarbons. 100 grms. distilled under atmospheric pressure gave 8 grms. below 150°, and 27 grms., 150°–300°. The specific gravity of the lower distillate was 0.7673, and of the higher, 0.8457. In vacuum distillation, 9382 grms. of the crude oil gave the following weights: —

–150° At. Pr.	–120°	120°–160°	160°–250°
123	865	1045	525

Nearly three-fourths of the original oil remained above 250°.

Continuing the distillation of the lower distillates within 5° and 2°, the following weights were collected: —

96°–100°	116°–120°	158°–160°	168°–170°	180°–182°
37	10	12	20	10 Grms.

In continuing the distillation of the lower fractions nothing came over below 60°, and only in quantities of a few grams below 95°.

HEPTAMETHYLENE, C_7H_{14}.

The fraction 98°–100° unpurified gave as its specific gravity at 20°, 0.7444, and after treatment with fuming sulphuric acid and sodic hydrate, 0.7414. A combustion of the purified oil gave the following percentages of carbon and hydrogen: —

0.1525 grm. of the oil gave 0.4797 grm. CO_2 and 0.1976 grm. H_2O.

	Calculated for C_7H_{14}.	Found.
C	85.70	85.53
H	14.30	14.40

As in the other oils, much benzol was contained in the fractions near 80°, and toluol in those near 110°.

OCTONAPHTENE, C_8H_{16}.

The fraction 118°–120° gave as its specific gravity unpurified at 20°, 0.7632, and after treatment with fuming acid and sodic hydrate, 0.7600. Specific gravity of octonaphtene, 0.7582. This distillate gave after purification, 86.62 per cent of carbon, and 14.60 per cent of hydrogen, which with its boiling point showed it to be octonaphtene.

To ascertain whether nonane is a constituent of Adams' Cañon oil, the distillate 148°–150° was determined, and found to be 0.7858. After treatment with the fuming acid and sodic hydrate its specific gravity was but slightly changed, 0.7800. A combustion then gave 86.10 per cent of carbon, and 13.91 per cent of hydrogen.

Since nonane requires 84.37 per cent of carbon and 15.63 per cent of hydrogen, it is evident that this hydrocarbon is not a constituent of Adams' Cañon oil.

DEKANAPHTENE, $C_{10}H_{20}$.

The unpurified distillate 158°–160° gave as its specific gravity at 20°, 0.7972, and 0.7904 after treatment with the fuming acid and sodic hydrate. A combustion of the purified oil gave the following percentages of carbon and hydrogen: —

0.1455 grm. of the oil gave 0.4583 grm. CO_2 and 0.1804 grm. H_2O.

	Calculated for $C_{10}H_{20}$.	Found.
C	85.70	85.91
H	14.30	13.78

The low percentage of hydrogen and high percentage of carbon indicates that the benzol homologue was not completely removed. In some of these distillates, the benzol hydrocarbon is present in such large proportion that long continued action of the fuming acid is necessary to remove it completely.

The small amount of the distillate 180°–182° gave as its specific gravity at 20°, 0.8154, and after treatment with the fuming acid, 0.8097. A combustion of the treated oil gave 85.56 per cent of carbon and 13.95 per cent of hydrogen. No further examination was made of the fractions collected under atmospheric pressure. Like the Bardsdale oil, part of the distillates between 140° and 220° under 50 mm. turned pink soon after they were collected, and on standing deposited a dark colored oil.

While the possibility of hydrocarbons poorer in hydrogen, such as condensed naphtene, is suggested by the low percentage of hydrogen, on account of the very large proportion of aromatic derivatives of benzol contained in Adams' Cañon oil, it seems more probable that these results are due to benzol derivatives not wholly removed, especially as the boiling points of the double ring naphtenes undoubtedly are much higher. Such a double ring naphtene apparently formed as one of the products by the action of sodium on monochlorheptamethylene boiled in the vicinity of 240°.

Torrey Wells Oil.

The specimen of petroleum from the Torrey wells was much lighter than that from Adams' Cañon; its specific gravity at 20° was 0.8837. It contained 0.49 per cent of sulphur, and gave 0.38 per cent of nitrogen by the Kjeldahl method and 1.15 per cent by volume. A combustion gave 86.00 per cent of carbon, and 12.48 per cent of hydrogen; 100 grms. distilled under atmospheric pressure gave 11 grms. with a specific gravity 0.7519 below 150°, and 29 grms. specific gravity 0.8226 between 150° and 250. In distilling Torrey oil *in vacuo*, 9860 grms. gave the following weights: —

-160° At. Pr.	-125°	125°–175°	175°–225°	225°–275°
655	790	1175	900	700 Grms.

Further distillation of the lower fractions gave, after the fourth distillation, the following weights, with smaller proportions at temperatures between: —

96°-98°	116°-120°	136°-140°	158°-162°	168°-171°	178°-182°
78	40	45	37	43	35 Grms.

The Torrey oil contained more of the lower distillates than any other of the specimens examined. Several grams collected below 40°, and at 65°–70°, 30 grams came together. The unpurified distillate 65°–70° gave as its specific gravity at 50°, 0.6981, which was reduced only to 0.6926 after agitation with fuming sulphuric acid. The specific gravity of hexane boiling at 68° is 0.6630.

Analysis of the purified oil gave the following results: —

I. 0.1551 grm. of the oil gave 0.4768 grm. CO_2 and 0.2138 grm. H_2O.
II. 0.1995 grm. of the oil gave 0.6146 grm. CO_2 and 0.2769 grm. H_2O.
III. 0.1369 grm. of the oil gave 0.4248 grm. CO_2 and 0.1888 grm. H_2O.

	Calculated for		Found.		
	C_6H_{12}.	C_6H_{14}.	I.	II.	III.
C	85.70	83.72	83.85	83.93	84.63
H	14.30	16.28	15.32	15.41	15.33

In analysis III. every precaution was taken to avoid loss of the oil after weighing, and the temperature of the combustion was maintained as high as the tube would stand. Probably the coincidence in the percentages of hydrogen is due to retention of unsaturated hydrocarbons in the sulphuric acid.

Apparently, as in the Fresno oil, the hydrocarbon at 68° is a mixture of hexane and hexamethylene.

Heptamethylene, C_7H_{14}.

The fraction 96°–98° had the specific gravity at 20°, 0.7496, which was scarcely changed by treatment with fuming sulphuric acid, 0.7430. Analysis I. was made of the crude distillate, and analysis II. of the purified product: —

I. 0.1222 grm. of the oil gave 0.3810 grm. CO_2 and 0.1602 grm. H_2O.
II. 0.1530 grm. of the oil gave 0.4801 grm. CO_2 and 0.1974 grm. H_2O.

	Calculated for	Found.	
	C_7H_{14}.	I.	II.
C	85.70	84.97	85.60
H	14.30	14.56	14.34

This product is, therefore, fairly pure heptamethylene.

The fractions in the vicinity of 110° were shown to be composed for the most part of toluol by the formation of nitro-products.

OCTONAPHTENE, C_8H_{16}.

The specific gravity of the crude distillate 118°–120° was 0.7598, and after purification with fuming sulphuric acid and sodic hydrate, 0.7530. A combustion of the unpurified oil gave 86.21 per cent of carbon and 13.35 per cent of hydrogen.

A combustion after purification indicated octonaphtene, although the percentage of hydrogen is somewhat too high, probably on account of accidental moisture: —

0.1470 grm. of the oil gave 0.4598 grm. CO_2 and 0.1976 grm. H_2O.

	Calculated for C_8H_{16}.	Found.
C	85.70	85.34
H	14.30	14.93

The distillates 135°–140° consisted largely of the xylols.

DEKANAPHTENE, $C_{10}H_{20}$.

The specific gravity of the crude fraction 158°–160° was 0.7742, and after purification with the fuming acid and sodic hydrate, 0.7742. Carbon and hydrogen were determined in the purified oil: —

0.1455 grm. of the oil gave 0.4583 grm. CO_2 and 0.1804 grm. H_2O.

	Calculated for $C_{10}H_{20}$.	Found.
C	85.70	85.91
H	14.30	13.78

The specific gravity of the crude distillate 168°–170° was 0.7928, and 0.7840 after treatment with fuming acid and sodic hydrate. A combustion of the purified oil gave 85.98 per cent of carbon and 13.69 per cent of hydrogen.

The fraction 178°–182° had the specific gravity before treatment, 0.8006, and afterward, 0.7924. A combustion of the oil after treatment gave 85.97 per cent of carbon and 13.51 per cent of hydrogen. The fraction 198°–200° had the specific gravity of 0.8133, and after treatment, 0.8069. The following percentages of carbon were given by combustion: carbon, 86.51; hydrogen, 13.54.

The low proportions of hydrogen and high proportions of carbon alluded to before are especially apparent in the Torrey oil. Whether this be due to a higher series or to benzol homologues not easily

removed will appear later in the composition of the higher vacuum distillates.

The Torrey distillates 140°–220°, 50 mm., showed a larger proportion of oxygen and nitrogen compounds than any other of the crude oils.

Scott's Hill (Sespe District) Oil.

The specimen of petroleum from Scott's Hill was lighter than the Torrey oil; its specific gravity at 20° was 0.8782. It contained 1.25 per cent of nitrogen. Two determinations of sulphur gave (I.) 0.38 and (II.) 0.49 per cent. 8260 grms. of the crude oil gave the following weights on distillation *in vacuo*: —

-150° At. Pr.	-160°	160°-208°	208°-275°
1220	495	930	880

The distillate –150° was collected under atmospheric pressure, the others under 70 mm. The portion –150° was subjected to further distillation collecting at first within 5°, and twice within 2°. The fractions collected in larger quantities within the following limits: —

66°-70°	86°-90°	96°-100°	116°-120°	136°-140°	156°-160°	170°-174°	178°-182°	190°-192°
26	38	35	37	38	62	41	38	41

Continuing the distillation of the higher fractions *in vacuo*, after the third distillation within limits of 2°, the larger quantities collected within the following limits with smaller quantities between:—

144°-148°	164°-168°	182°-186°	210°-214°
60	55	65	23

In distilling corresponding fractions from other fields *in vacuo* a tendency to collect within the same limits was observed. After agitation with fuming sulphuric acid, the fraction 66°–70° atmospheric pressure gave as its specific gravity at 20°, 0.6984; the specific value much higher than the specific gravity of hexane, 0.6630(17°5). A combustion gave percentages of carbon and hydrogen corresponding to a mixture of hexamethylene and hexane: —

	Calculated for		Found.
	C_6H_{12}.	C_6H_{14}.	
C	85.70	83.72	84.67
H.	14.30	16.28	15.15

The distillates 65°–70° from Torrey, Scott's Hill, and Fresno oils were put together and carefully distilled a number of times in order to separate so far as possible the hydrocarbon boiling at 68° or 69° from other admixtures, and the fraction 68°–69° was thoroughly treated with fuming sulphuric acid, warming gently and allowing it to stand with the acid over night. Before treatment the specific gravity at 20° was 0.7005, and after treatment, 0.6929. The following results were obtained by analysis: —

I. 0.2422 grm. of the oil gave 0.7596 grm. CO_2 and 0.3234 grm. H_2O.

	Calculated for		Found.
	C_6H_{12}.	C_6H_{14}.	I.
C	85.70	83.72	85.50
H	14.30	16.28	14.84

In this analysis the combustion tube was filled with oxygen before the oil was volatilized, and the temperature was kept as high as the tube would stand. There seems therefore to be little doubt that the hydrocarbon in California petroleum boiling at 68°–69° is composed chiefly of hexamethylene.

Since small quantities of distillates remained in the vicinity of 90°–91°, it suggested the possibility that isoheptane might form a part of this product. But its high specific gravity, 0.7303 at 20°, isoheptane 0.6819 (17°.5), and the composition showed by analysis, excluded isoheptane in any considerable quantity.

0.1273 grm. of the oil gave 0.3987 grm. CO_2 and 0.1665 grm. H_2O.

	Calculated for		Found.
	C_7H_{14}.	C_7H_{16}.	
C	85.70	84.00	85.40
H	14.30	16.00	14.53

Especial precautions were taken in this analysis to have the temperature of the combustion as hot as possible, and the tube was filled with oxygen before the oil volatilized. The proportions of carbon and hydrogen indicating the absence of isoheptane could not have been due to the presence of benzol, since the oil was treated several times with fuming sulphuric acid. The volatile portions of California petroleum, therefore, contain at most very small proportions of the hydrocarbons, C_nH_{2n+2}, and these if present consist almost exclusively of members below normal hexane. Further confirmation of these formulae is given by the chlorine derivatives, which will be described in another paper.

HEPTAMETHYLENE, C_7H_{14}.

The fraction 96°–98° gave as its specific gravity at 20°, 0.7479, and after purification with fuming sulphuric acid, 0.7436. A combustion of the purified oil gave the following results: —

0.1530 grm. of the oil gave 0.4801 grm. CO_2 and 0.1974 grm. H_2O.

	Calculated for C_7H_{14}.	Found.
C	85.70	85.60
H	14.30	14.34

These values leave no doubt that this constituent was heptamethylene.

OCTONAPHTENE, C_8H_{16}.

A determination of the specific gravity of the fraction 118°–120° at 20° gave 0.7628, and after agitation with fuming acid and sodic hydrate, 0.7569. Determinations of carbon and hydrogen were made both before and after purification.

I. 0.1644 grm. of the unpurified oil gave 0.5196 grm. CO_2 and 0.1975 H_2O.

II. 0.1470 grm. of the purified oil gave 0.4600 grm. CO_2 and 0.1976 grm. H_2O.

	Calculated for C_8H_{16}.	Found. I.	Found. II.
C	85.70	86.21	85.34
H	14.30	13.35	14.93

Although all these oils were dried over sodium, the hydrogen in analysis II. is somewhat too high, probably on account of a trace of moisture.

No further examination of the higher fractions of this oil below 160° was made, except of the portions collected at 135°–140°, to show that large proportions of the xylols were contained as in the other specimens examined.

DEKANAPHTENE, $C_{10}H_{20}$.

The specific gravity of the fraction 158°–160° was found to be 0.7848, and after agitation with the fuming acid, 0.7751. The proportions of carbon and hydrogen were determined by analysis: —

I. 0.1444 grm. of the oil gave 0.4575 grm. CO_2 and 0.1885 grm. H_2O.
II. 0.1451 grm. of the oil gave 0.4533 grm. CO_2 and 0.1848 grm. H_2O.

	Calculated for $C_{10}H_{20}$.	Found. I.	II.
C	85.70	85.65	85.24
H	14.30	14.22	14.33

UNDEKANAPHTENE, $C_{11}H_{22}$.

The specific gravity of this fraction without purification was 0.8093 at 20°, and after treatment with the fuming acid and sodic hydrate, 0.7952. A combustion gave the following percentages of carbon and hydrogen:—

0.1458 grm. of the oil gave 0.4593 grm. CO_2 and 0.1817 grm. H_2O.

	Calculated for $C_{11}H_{22}$.	Found.
C	85.70	85.90
H	14.30	13.85

Assuming, which is probable, that the benzol homologue was completely removed, these proportions of carbon and hydrogen point to the presence of a hydrocarbon of a series containing less hydrogen.

A similar result was obtained with the fraction 194°–196°, specific gravity crude, 0.8145, and after treatment, 0.8022. Combustion of the purified oil gave the following percentages: —

	I.	II.
C	85.52	85.85
H	13.97	13.92

While the percentages of carbon in these analyses are satisfactory for the formula C_nH_{2n}, the percentages of hydrogen are less satisfactory. The deficiency of about one half of one per cent in the sum of the carbon and hydrogen has appeared in many of the analyses of products that could be reasonably accepted as to their formula. With the greatest care in the details of analysis, we have also found difficulty in obtaining the total carbonic dioxide evolved by combustion of the oil in the ordinary method of analysis. This subject has received attention in another paper on this method of analysis.

TRIDEKANAPHTENE, $C_{13}H_{26}$.

After the separation of distillates *in vacuo* from the crude oils, the fractions may be distilled at temperatures which would cause decomposi-

tion of constituents of the crude oil. It is therefore possible to continue the distillation of the hydrocarbons even as high as tridekanaphtene under atmospheric pressure after the first distillation. In continuing the distillation, 35 grams collected at 230°–232°, specific gravity 0.8511. After purification with fuming sulphuric acid it gave as its specific gravity 0.8134 at 20°. A combustion gave the following results: —

0.1511 grm. of the oil gave 0.4733 grm. CO_2 and 0.1937 grm. H_2O.

	Calculated for $C_{13}H_{26}$.	Found.
C	85.70	85.41
H	14.30	14.24

This formula was also verified by a determination of its molecular weight: —

1.2712 grm. of the oil and 25.24 grms. benzol gave a depression of 1°.370.

Calculated for $C_{13}H_{26}$.	Found.
182	180

A determination of the index of refraction gave 1.4745, and the molecular refraction 60.254; calculated for $C_{13}H_{26}$, 59.839.

TETRADEKANAPHTENE, $C_{14}H_{28}$.

A considerable quantity of distillate collected at 144°–146°, which gave as its specific gravity before purification 0.8428, and after purification 0.8154. A combustion gave percentages of carbon and hydrogen required for the formula C_nH_{2n}.

0.1462 grm. of the oil gave 0.4600 grm. CO_2 and 0.1824 grm. H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.70	85.81
H	14.30	13.87

A determination of molecular weight at the freezing point gave a value required for tetradekanaphtene: —

1.3356 grm. of the oil and 24.22 grms. benzol gave a depression of 1°.394.

Calculated for $C_{14}H_{28}$.	Found.
196	194

The index of refraction of this hydrocarbon was found to be 1.4423, and the molecular refraction 63.75; required for $C_{14}H_{28}$, 64.44.

Pentadekanaphtene, $C_{15}H_{30}$.

From each of the California oils, distillates *in vacuo* collected at 160°–162°, 50 mm., corresponding nearly to 260°–262°, atmospheric pressure. The specific gravity of the fraction from Scott's Hill oil was 0.8600, and after purification with fuming sulphuric acid, 0.8171. A combustion gave the following values for carbon and hydrogen: —

0.1454 grm. of the oil gave 0.4558 grm. CO_2 and 0.1829 grm. H_2O.

	Calculated for $C_{15}H_{30}$.	Found.
C	85.70	85.47
H	14.30	13.97

The percentages of carbon and hydrogen in the analysis of the two hydrocarbons last described indicate a falling off in the proportions of hydrogen. The deficiency in the analysis is more probably due to loss of carbonic dioxide than of water. Similar variations have been noted in connection with some of the lower hydrocarbons in other crude California oils. The deficiency in hydrogen may indicate, as mentioned heretofore, the presence of hydrocarbons composed with more than one methylene ring, which would require prolonged distillation for their complete removal. From the heavier California oils composed, it appears, largely of asphaltic hydrocarbons, the falling off in the proportion of hydrogen and consequent increase in carbon indicates the presence of hydrocarbons with the formula C_nH_{2n-2}. Such differences do not appear in determinations of molecular weights, but are shown by analysis.

There are wide variations in the specific gravity of the distillates of California oil above 230° from different sources. This may indicate a certain proportion of hydrocarbons of a lower series than C_nH_{2n}, and the higher percentages of carbon and lower percentages of hydrogen in some of these oils indicate the possibility of hydrocarbons C_nH_{2n-2}.

For faithful assistance in this work the following gentlemen should receive credit: Messrs. Shaw, Ames, Richards, Cushing.

From this examination of California petroleum, the following conclusions may be drawn: —

An essential characteristic is the relatively small proportions of the distillates below 225°. The main body of the crude oils from the principal fields distilling below 225° is composed of methylenes which resemble those identified in Russian oil, in boiling points and in specific gravity, except undekanaphtene, $C_{11}H_{22}$, dodekanaphtene, $C_{12}H_{24}$, and tridekanaphtene, $C_{13}H_{26}$, which differ in boiling points. The proportion of the

aromatic hydrocarbons is much larger, apparently, in California oil. The homologues of benzol form a considerable proportion of the distillates, especially of those with lower boiling points. In the distillate 221°–222° from Puente oil so much naphtalene was present that the distillate became solid at 0°.

California petroleum differs totally from the Eastern oils, — Pennsylvania, Ohio, Canadian, etc., — and also materially from Russian oil, in not containing members of the series C_nH_{2n+2}. In this respect, and in respect to the large proportion of aromatic hydrocarbons, California petroleum is unlike any other petroleum that has been examined in this Laboratory. Incidentally it may be mentioned that California petroleum differs from other petroleums hitherto examined in the large proportions of oxygen and nitrogen compounds which it contains. These bodies are under investigation in this Laboratory.

Study of the portions with high boiling points, which is now in progress, will have an especial interest, since, when they are separated without decomposition, they form the most valuable constituents of lubricating oils and asphalts that have been separated from petroleum. In some of the high distillates, such as those from Summerland oil, hydrocarbons of the series C_nH_{2n-2} and the series C_nH_{2n-4} have been identified.

No. 36. — ON THE CHLORINE DERIVATIVES OF THE HYDROCARBONS IN CALIFORNIA PETROLEUM.

By Charles F. Mabery and Otto J. Sieplein.

In further confirmation of the composition of the hydrocarbon 68°–70° described in the previous paper (Mabery and Hudson), the chlorine derivatives were formed by exposing the hydrocarbon over water to the action of chlorine, in ordinary daylight. After washing and drying, the chlorine product was fractioned under atmospheric pressure until it collected at 125°–130°, and for the most part at 126°. It distilled constant under normal conditions with the mercury all in the vapor at 125°.5.

The specific gravity at $\frac{20°}{20°}$ was 0.9255; at $\frac{20°}{40°}$, 0.9239; at $\frac{30°}{40°}$, 0.9143; and at $\frac{40°}{40°}$, 0.9044. The coefficient of expansion calculated from the average of these determinations is 0.000918.

A chlorine determination gave the following percentage: —

0.1572 grm. of the oil gave 0.1872 grm. AgCl.

	Calculated for $C_6H_{11}Cl$.	Found.
Cl	29.92	29.50

The molecular weight was determined at the freezing point of benzol. 1.1641 grm. of the oil and 19.92 grm. benzol gave a depression of 2°.482.

Calculated for $C_6H_{11}Cl$.	Found.
118.5	118

The index of refraction at 20° was found to be 1.416, and the molecular refraction, 33.29. Required for $C_6H_{11}Cl$, 32.54. Hexamethylene is, therefore, the principal hydrocarbon with this boiling point.

In distilling the portions of California petroleum below 100°, it has always been observed that a distillate collected at 90°–91°. To ascertain whether a hydrocarbon were really present with this boiling point, distillation of the fractions 85°–100° was continued through a tall Hempel column until a larger portion collected at 89°–90°. The specific gravity of this fraction without purification was 0.7295, $\frac{20°}{20°}$. After thorough treatment first with common sulphuric acid, then with fuming acid, the specific gravity was not changed, 0.7295. The index of refraction of this hydrocarbon at 20° was 1.411, and the molecular refraction 33.35; calculated for C_7H_{14}, 32.22. The molecular weight at the freezing point was found to be as follows: —

0.8669 grm. of the oil and 17.62 grms. of benzol gave a depression 2°.547.

Calculated for C_7H_{14}.	Found.
98	99

With the mercury column all in the vapor, Bar. 745.3 mm., this hydrocarbon distilled completely at 90°.4.

The chlorine derivative of this hydrocarbon was formed by the action of chlorine over water. After washing, drying, and distillation under atmospheric pressure, the chloride came together at 145°–150°, for the most part at 147°.

A determination of chlorine gave a value required for the monochloride: —

0.1605 grm. of the oil gave 0.1696 grm. AgCl.

	Calculated for $C_7H_{13}Cl$.	Found.
Cl	26.77	26.13

The specific gravity of the chloride at $\frac{20°}{20°}$ was 0.9332; at $\frac{20°}{40°}$, 0.9316; at $\frac{30°}{40°}$, 0.9231; at $\frac{40°}{40°}$, 0.9138. The coefficient of expansion for one degree calculated from these results is 0.000973.

A determination of the molecular weight at the freezing point gave the following value: —

0.9318 grm. of the oil and 19.98 grms. of benzol gave a depression of 1°.744.

Calculated for $C_7H_{13}Cl$.	Found.
132.5	131

The index of refraction at 20° was found to be 1.441, and the molecular refraction, 37.57; calculated for $C_7H_{13}Cl$, 37.11.

These results are sufficient to establish the formula for this hydrocarbon as C_7H_{14}. It is probably dimethylpentamethylene. It differs in its properties from methylhexamethylene, boiling point 99°–100°; its chloride boils at 147°, while methylhexamethylene chloride boils at 141°–142°.

Methylhexamethylene Chloride, $C_7H_{13}Cl$.

To ascertain the correct boiling point of heptamethylene, the distillates 95°–100° were carried through a series of distillations until the greater portion collected at 98°–100°, and this product distilled for the most part at 99°–100°, Bar. 745°.3, with the mercury column wholly in the vapor.

The empirical formula of this hydrocarbon has been ascertained in the distillates from various specimens of California oils, by analysis and determinations of molecular weight. The boiling point of hexahydrotoluol, prepared by the addition of hydrogen to toluol, was given as 97°. Markownikoff found that the same hydrocarbon separated from Russian petroleum, and also the synthetically prepared heptanaphtene, boiled at 101°.

For further identification of our product it seemed advisable to study its derivatives. The chlorine derivative was first formed by passing chlorine into the hydrocarbon over water until the greater part was converted into the chloride. This reaction takes place very readily in

ordinary daylight, and with a large generator the action of chlorine may be made continuous, saving much time in the chlorination. This method seems to be more advantageous than that formerly used by us in which dry chlorine was allowed to act on the vapor of the dry oil. The chlorinated oil was washed, dried over calcium chloride, and fractioned. After five distillations through a Hempel column, a considerable portion collected at 141°–142°, which proved to be the monochloride, and more remained above 160°, which was doubtless the dichloride.

A determination of chlorine in the fraction 141°–142° by the method of Carius gave a value required for $C_7H_{18}Cl$: —

0.1863 grm. of the oil gave 0.2025 grm. AgCl.

	Calculated for $C_7H_{13}Cl$.	Found.
Cl	26.77	26.88

The molecular weight was also determined by the Beckman freezing point method: —

1.1960 grm. of the oil and 25.8960 grms. benzol gave a depression of 1°.701.

Calculated for $C_7H_{13}Cl$.	Found.
132.5	133

The specific gravity of the monochloride at 20° was found to be 0.9310. For further confirmation of the formula, the index of refraction was determined with the aid of a Pulfrich refractometer, and from the density and molecular weight the molecular refraction was calculated. The index of refraction found was 1.441, and the molecular refraction: —

Calculated for $C_7H_{13}Cl$.	Found.
37.11	37.57

The theoretical value was calculated on the assumption that all the carbons are singly connected.

In order to ascertain whether the chlorine atom enters the ring or side chain, the nitril was formed by heating the chloride with alcoholic potassic cyanide for several hours. There was an abundant separation of potassic chloride, and on diluting the solution the nitril separated as an oily liquid above the water. This oil had the characteristic odor of the nitrils. Its specific gravity at 20° was 0.9253, and its index of refraction, 1.45. The molecular refraction, assuming the molecular weight, was

35.78, calculated from the elements, assigning to the cyanogen group the value 5.33, which was determined from ethyl cyanide, C_2H_5CN. The theoretical molecular refraction for the nitril calculated on the same basis is 36.45.

The nitril was saponified by heating it to 110° with concentrated hydrochloric acid. The acid formed had the odor of alphatoluic acid, but the amount obtained was not sufficient for complete examination.

When heptamethylene chloride was brought together with metallic sodium, a vigorous action soon set in with the evolution of great heat, sufficient to cause the decomposition of the products unless it was controlled by cooling. This reaction was best carried on by dissolving the chloride in ether, adding the sodium in slight excess over the calculated amount, and keeping the solution cold. In two hours the reaction was complete. The products included an unsaturated hydrocarbon, boiling point 97°, and another hydrocarbon, boiling point approximately 220°–230°. That the hydrocarbon boiling at 97° was unsaturated was shown by the formation of a bromine addition product; bromine added readily in the cold with no escape of hydrobromic acid. A Carius determination of the bromine in this product gave the following result:—

0.2045 grm. of the oil gave 0.3023 grm. AgBr.

	Calculated for $C_7H_{12}Br_2$.	Found.
Br	62.5	62.9

The specific gravity of the dibrom-derivative at 20° was 1.648. A determination of its molecular weight was made:—

0.9238 grm. of the oil and 25.3 grms. of benzol gave a depression of 0°.725.

Calculated for $C_7H_{12}Br_2$.	Found.
256	247

The odor of the unsaturated hydrocarbon was very sharp and penetrating, very different from that of the paraffine and methylene hydrocarbons, but resembling the olefines. In further proof that it contained doubly bonded carbon, it was titrated with the Hübl reagent, an alcoholic solution of iodine and mercuric chloride. The amount of iodine absorbed was approximately equivalent to two atoms of iodine for each molecule of the hydrocarbon. When heated with hydriodic acid, the monoiodide was readily formed. The specific gravity of the unsaturated hydrocarbon

at 20° was 0.7472. Its molecular weight was ascertained by the freezing point method: —

0.7116 grm. of the oil and 25.19 grms. of benzol gave a depression of 1.420.

Calculated for C_7H_{12}.	Found.
96	98

The index of refraction with sodium light was found to be 1.416. The molecular refraction calculated from the density and molecular weight was: —

Calculated for		Found.
$C_6H_9CH_3$.	C_6H_{10}=CH_2.	
30.06	31.77	32.34

These values indicate that the unsaturated hydrocarbon contains a double bond between the side chain carbon and a carbon atom in the ring, confirming the position of the chlorine atom in the side chain which is indicated by the ease with which it is replaced in the reaction with potassic cyanide. The form that the chlorination takes doubtless depends on the fact that the hydrogen in the side chain is less firmly bound than the hydrogen atoms in the methylene ring. The unsaturated condition C_6H_{10}=CH_2 is shown by the action of halogens and haloid acids, and confirmed by the molecular refraction, which corresponds to the sum of the atomic refractions assuming the double bond.

This constituent of California petroleum is therefore identical with methyl hexamethylene, which may be formed by the addition of hydrogen to toluol.

The hydrocarbon with a boiling point 220°–230°, formed by the action of sodium on methyl hexamethylene chloride, doubtless contains two methylene rings: — $C_6H_{11}CH_2$-CH_2C_6-H_{11}. The quantity of this product formed was too small for identification, but it evidently affords a means for building up the higher methylene hydrocarbons containing more than one methylene ring. That it was a condensed hydrocarbon was shown by its high specific gravity, 0.8872.

Dimethylhexamethylene Chloride, $C_8H_{15}Cl$.

The formula of dimethylhexamethylene was ascertained, as shown in the previous paper, by analysis and determination of its molecular weight. The formula was still further verified by the formation of the chlorine derivative. As in the chlorination of methylhexamethylene, chlorine

was allowed to act on the hydrocarbon over water in ordinary daylight until it was nearly all converted into the chlorine derivative. After washing and drying, the product was distilled under atmospheric pressure; after several distillations the monochloride collected in larger part at 168°–170°. The specific gravity of this product at 20° was found to be 0.9358. A determination of chlorine gave the following result: —

0.2034 grm. of the oil gave 0.1973 grm. AgCl.

	Calculated for $C_8H_{15}Cl$.	Found.
Cl	24.21	24.01

The molecular weight of the chloride was determined by the freezing point method.

0.7293 grm. of the oil and 25.66 grms. benzol gave a depression of 0°.982.

Calculated for $C_8H_{15}Cl$.	Found.
146.5	142

The index of refraction in sodium light at 20° was 1.455, and the molecular refraction: —

Calculated for $C_8H_{15}Cl$.	Found.
41.69	41.60

That the chlorine enters a side chain in this reaction, as in the case of methylhexamethylene, appears from the ready formation of the nitril by heating the chloride with alcoholic potassic cyanide. On diluting the solution the nitril separated as an oil, with the characteristic odor of the nitrils. It was saponified by heating with aqueous potassic hydrate. On acidifying the solution, a solid was precipitated, with an odor characteristic of the alpha-toluic acids; but the quantity obtained was not sufficient for identification. It was probably meta-methyl, alpha-toluylic acid.

Trimethylhexamethylene Chloride, $C_9H_{17}Cl$.

This chloride was also formed, washed, dried, and fractioned under atmospheric pressure. It came together in larger quantity at 186°–188°; its specific gravity at 20° was 0.9380. The percentage of chlorine was determined.

0.2300 grm. of the oil gave 0.2041 grm. AgCl.

	Calculated for $C_9H_{17}Cl$.	Found.
Cl	22.10	21.94

The molecular weight was also ascertained at the freezing point.

0.8672 grm. of the oil and 25.03 grms. benzol gave a depression of 1°.090.

Calculated for $C_9H_{17}Cl$.	Found.
160.5	156

In further support of the formula of the chloride, the index of refraction was determined, 1.462, and the molecular refraction calculated.

Calculated for $C_9H_{17}Cl$.	Found.
46.8	47

When sodium was allowed to act on trimethylhexamethylene chloride, a vigorous reaction set in that could be controlled by cooling. By carrying on the reaction in an ethereal solution, on standing over night in water the reaction was complete. The product of the reaction consisted for the most part of an unsaturated hydrocarbon, and a smaller quantity of a heavy oil, doubtless formed by the union of two methylene rings. The boiling point of the unsaturated hydrocarbon was 135°–140°. Its unsaturated condition was shown by the readiness with which it united with iodine in Hübl's reagent, absorbing approximately two atoms of iodine. The specific gravity of the unsaturated hydrocarbon at 20° was 0.7762. The molecular weight at the freezing point was determined.

0.8572 grm. of the oil and 22.45 grms. benzol gave a depression of 1°.571.

Calculated for C_9H_{16}.	Found.
124	120

The index of refraction was found to be 1.431, and the molecular refraction: —

Calculated for		Found.
$C_6H_7(CH_3)_3$.	$C_6H_8(CH_3)_2{=}CH_2$.	
39.26	40.97	41.46

Dekanaphtene Chloride, $C_{10}H_{19}Cl$.

In confirmation of the formula of dekanaphtene, the index of refraction was determined and the molecular refraction calculated. With the density 0.7898, and the index 1.4325, the molecular weight gave the following value: —

Calculated for $C_{10}H_{20}$.	Found.
46.10	46.00

The chlorine derivative of this hydrocarbon was formed by passing in chlorine over water. After washing, drying, and fractioning *in vacuo*, the chloride collected in larger quantities at 105°–110° (50 mm.) Another portion collected at 140°–145°, probably a dichloride. The specific gravity of the monochloride at 20° was 0.9470. A determination of chlorine gave the following value: —

0.1840 grm. of the oil gave 0.1476 grm. AgCl.

	Calculated for $C_{10}H_{19}Cl$.	Found.
Cl	20.33	19.80

The molecular weight of the chloride at the freezing point of benzol was also determined: —

1.2536 grm. of the oil and 21.29 grms. benzol gave a depression of 1°.689.

Calculated for $C_{10}H_{19}Cl$.	Found.
174.5	171

A determination of the index of refraction of this chloride gave 1.468. The molecular refraction calculated as follows: —

Calculated for $C_{10}H_{19}Cl$.	Found.
50.89	51.34

On account of the small quantity of the dichloride obtained, it was not possible to purify it completely by distillation. But a determination of chlorine gave 31.53 per cent; required for $C_{10}H_{18}Cl_2$, 33.90. A determination of molecular weight gave 199; required for the dichloride, 209. The molecular refraction calculated from the index was 56.98; calculated from the formula, 55.81. On account of the differences between the theoretical values for the mono- and di-chlorides, these values are sufficient to show that the dichloride was formed and separated in nearly a pure form.

Undekanaphtene Chloride, $C_{11}H_{21}Cl$.

The index of refraction of this hydrocarbon was found to be 1.4403, and the molecular refraction: —

Calculated for $C_{11}H_{22}$.	Found.
50.70	50.63

This determination was made in the distillate 190°–192°, which was used for all work on this hydrocarbon.

The chlorine derivative was prepared in the same manner as those of the hydrocarbons previously described. On fractioning it *in vacuo* at 35 mm. it collected for the most part at 125°–130°. Its specific gravity was found to be 0.9583 at 20°. A chlorine determination supported the formula of the monochloride.

0.1560 grm. of the oil gave 0.1179 grm. AgCl.

Calculated for $C_{11}H_{21}Cl$.	Found.
18.81	18.69

The molecular weight was determined at the freezing point of benzol.

0.6055 grm. of the oil and 17.37 benzol gave a depression of 0°.890.

Calculated for $C_{11}H_{21}Cl$.	Found.
188.5	192

The index of refraction was found to be 1.476, and the molecular refraction: —

Calculated for $C_{11}H_{21}Cl$.	Found.
55.48	54.32

The composition of its chloride, together with its molecular weight and molecular refraction, all show that undecane has for its boiling point 194°–196.°

DODEKANAPHTENE CHLORIDE, $C_{12}H_{23}Cl$.

The index of refraction of dodekanaphtene was found to be 1.4649, and the molecular refraction: —

Calculated for $C_{12}H_{24}$.	Found.
55.38	55.24

The chlorine derivative was formed, washed, dried, and fractioned *in vacuo.* It collected for the most part at 130°–135° (17 mm.) Its specific gravity at 20° was 0.9616. A determination of chlorine gave the following result: —

0.1657 grm. of the oil gave 0.1153 grm. AgCl.

	Calculated for $C_{12}H_{23}Cl$.	Found.
Cl	17.52	17.20

The molecular weight was also determined: —

0.7172 grm. of the oil and 19.04 grms. benzol gave a depression of 0.925.

Calculated for $C_{12}H_{23}Cl$.	Found.
202.5	204

The index of refraction was 1.480, and the molecular refraction: —

Calculated for $C_{12}H_{23}Cl$.	Found.
60.77	59.96

TRIDEKANAPHTENE CHLORIDE $C_{13}H_{25}Cl$.

The index of refraction of this hydrocarbon as determined is 1.4745, and its molecular refraction: —

Calculated for $C_{13}H_{26}$.	Found.
60.25	59.84

The chlorine derivative was formed by the action of chlorine, dried and fractioned under 17 mm.; it came together for the most part at 140°–145°. Its specific gravity at 20° was 0.9747; a Carius determination gave the following percentage of chlorine: —

0.1674 grm. of the oil gave 0.1137 grm. AgCl.

Calculated for $C_{13}H_{25}Cl$.	Found.
16.38	16.78

In the chlorine derivatives of the higher hydrocarbons the weight of oil that can be taken for analysis is limited, since as in the last analysis the pressure of the large volume of gases formed is more than the tube can stand. The molecular weight of tridekanaphtene chloride was determined at the freezing point of benzol: —

0.4447 grm. of the oil and 17.88 grms. benzol gave a depression of 0.763.

Calculated for $C_{13}H_{25}Cl$.	Found.
216.5	217

TETRADEKANAPHTENE CHLORIDE, $C_{14}H_{27}Cl$.

Tetradekanaphtene chloride was readily formed by passing chlorine into the hydrocarbon over water in ordinary daylight; if the action was stopped with a small portion of the hydrocarbon unacted on, the product consisted for the larger part of the monochloride. After washing and drying, the chlorine derivative was separated by continued distillation *in*

vacuo under 13 mm.; it came together for the most part at 150°–155°. The specific gravity of the monochloride was 0.9748 $\frac{20^\circ}{20^\circ}$; at $\frac{20^\circ}{4^\circ}$ 0.9730; at $\frac{20^\circ}{40^\circ}$, 0.9661; and at $\frac{40^\circ}{40^\circ}$, 0.9579. The mean coefficient of expansion, within 20°–40°, from these results, is 0.00078.

A determination of chlorine gave a value required for the monochloride: —

0.1559 grm. of the oil gave 0.0989 grm. AgCl.

	Calculated for $C_{14}H_{27}Cl$.	Found.
Cl	15.39	15.80

As mentioned above, the decreasing proportion of chlorine in these derivatives with the increasing molecular weight, and the consequent larger volumes of gases, beyond the strength of the ordinary Carius tubes, gives a smaller weight of silver chloride than could be desired, but the accuracy of the method permits of sufficiently reliable results, even with the small weights.

The molecular weight of the chloride was determined at the freezing point of benzol: —

0.8923 grm. of the oil and 17.76 grms. benzol gave a depression of 1°.094.

Calculated for $C_{14}H_{27}Cl$.	Found.
230.5	225

The index of refraction was found to be, 1.493, and the molecular refraction 68.67; calculated for $C_{14}H_{27}Cl$, 69.37.

The boiling point of this chloride cannot be accurately determined under atmospheric pressure because it is rapidly decomposed at the higher temperature and in presence of air, although it may be distilled indefinitely *in vacuo*. Probably the boiling point under atmospheric pressure is not far from 275°.

Pentadekanaphtene Chloride, $C_{15}H_{29}Cl$.

This chloride was prepared from pentadekanaphtene, which had been well fractioned *in vacuo*. These higher chlorides are formed as readily as the lower ones. After washing and fractional distillation under 14 mm. this monochloride came together for the most part at 170°–175° without decomposition. Its boiling point under atmospheric pressure is probably near 300°. Its specific gravity at $\frac{20^\circ}{20^\circ}$ was 0.9771; at $\frac{20^\circ}{4^\circ}$ 0.9753; and at $\frac{20^\circ}{40^\circ}$, 0.9714; and at $\frac{40^\circ}{40^\circ}$, 0.9643. The coefficient of expansion calcu-

lated from these values is 0.000576. A Carius determination gave the required percentage of chlorine.

0.1536 grm. of the oil gave 0.0923 grm. silver chloride.

Calculated for $C_{15}H_{29}Cl$.	Found.
14.51	14.85

A determination of the molecular weight supported the same formula.

0.9073 grm. of the oil and 18.93 grms. benzol gave a depression of 0°.984.

Calculated for $C_{15}H_{29}Cl$.	Found.
239	244.5

The index of refraction was 1.493, and the molecular refraction, 72.90; calculated for $C_{15}H_{29}Cl$, 73.97.

Attempts will be made to form the chlorides of the higher hydrocarbons in connection with the study of the composition of these bodies.

No. 37. — ON THE COMPOSITION OF JAPANESE PETROLEUM.

By Charles F. Mabery and Shinichi Takano.*

The oil fields in Japan are the most promising and are under the most rapid development of any recently discovered oil territory. The output in 1891 was 56,000 bbls. annually; in 1899 it was 1,000,000 bbls. The oil territory in Japan is contained in the province of Echigo, at least to the extent of 90 per cent, on the northern coast of the Sea of Japan. This province is surrounded in part by a mountain chain which

* Mr. Takano has spent three years in the study of petroleum in this country, having been sent for this purpose by the Japanese Government. He is thoroughly familiar with the geology of the oil territory in Japan, having given especial attention to this subject in a thesis which he presented for a degree in the University of Tokio. Besides a thorough knowledge of the composition of petroleum from a chemical point of view, which he has gained during the two years he has spent exclusively in the study of this subject in this Laboratory, Mr. Takano spent one year as a laborer in different refineries, where he took charge by actual manipulation of every process in the preparation of commercial products. The work presented in this paper formed the subject of a thesis by Mr. Takano for the degree of M.S.

encloses a section of country 140 miles long by 150 miles broad, rising gradually from the sea to the mountains with a varying altitude from 150 feet to 500 feet. Oil is found chiefly in the Upper Eocene of the Tertiary formation, where it is held under pressure between impervious layers of slate and sandstone.

Nodules of calcite are frequently found embedded in the sandstone, and crystals of calcite twinned, resembling those found in the Ohio Trenton-limestone, oil-bearing rock. The oil strata are full of sea-shells, a good indication as to the origin of the oil formations. There are great variations in the depths of the wells. For example, the wells of the Amaze field are approximately 2000 feet in depth, while those of the Miyagawa field, only six miles distant, are 700 feet deep; the wells of the Niitsu field are still shallower, 600 feet. The Nagaoka wells are 800 feet in depth. Nevertheless the oil strata at the different depths are essentially of the same formation. The sandstone in which the Nagaoka oil is found is coarser than that of the other fields. On the surface of the Niitsu oil territory are immense beds of peat which are used for fuel.

Although the oil fields of Japan are situated in close proximity, specimens of oil from the different fields differ as essentially in composition as the variations in specific gravity indicate. As will appear later, the Amaze, Miyagawa, and Hirei fields yield paraffine in considerable quantities. While the hydrocarbons above C_7H_{14} do not include members of the series C_nH_{2n+2}, at least so far as it appears from analysis of distillates prepared on a laboratory scale, the lower distillates do contain members of the paraffine series.

The paraffine hydrocarbons with low boiling points, such as the butanes, pentanes, and hexanes, have an agreeable sweetish odor that is easily recognizable, and quite different from the pungent harsh odor of the methylenes. The odor of the paraffines is more apparent in the Miyagawa oil than in any other of the Japanese oils we have seen, and somewhat less in the Amaze oil. When these hydrocarbons with low boiling points are present, the crystalline paraffine hydrocarbons C_nH_{2n+2} are usually to be found.

Considerable quantities of gas were formerly obtained from the Amaze oil territory, but the supply now seems to be exhausted, at least so far as wells have been bored; some gas escapes from the shallow Miyagawa wells, more from the shallow wells of the Niitsu territory. As wells are sunk deeper in this territory it is probable that lighter oils will be found. On account of the friable condition of the oil rock and the danger of

clogging the wells by loose material, "shooting" the wells after boring is not practised. The flow from the wells is irregular; frequently it will amount to 300 barrels a day for a week, and then stop, and the oil must be pumped.

The oil territory in Japan includes the following fields: — Amaze, Nagaoka, Niitsu, and Hiyama. The different sections of the oil territory may be classified as follows: —

Amaze	Amaze Miyagawa Gendogi	green oil
Nagaoka	Hirei Kitatani Katsudo	dark oil
Niitsu	Koguchi Kusodsu	
Hiyama	Hiyama	dark green oil

The Amaze field is the oldest; the Hiyama field has been most recently developed; both these oils contain paraffine.

The crude oils from the different fields differ essentially in their properties, as shown by the different specific gravity, the different percentages

	Amaze.	Hirei.	Katsudo.	Kitatani.	Koguchi.	Kusodsu.	Miyagawa.
Specific Gravity . . .	0.8245	0.8622	0.8771	0.8952	0.9435	0.9210	0.8911
Per cent Sulphur . .	0.23	0.41	0.82	0.61	0.49	0.37	0.32
Per cent Nitrogen . .	0.35	0.74	0.07	0.75	1.34	1.23	0.55
Iodine Absorption . .	0.0	0.84	7.66	0.82	9.79	0.62	1.63
Coefficient of Expansion	82.5	78.5	76.5	79.5	67.5	61.5	74.5

PERCENTAGES OF DISTILLATES.

	Amaze.	Hirei.	Katsudo.	Kitatani	Koguchi.	Kusodsu.	Miyagawa.
– 150°	22. 8	21.8	22.2	14.	0.0	0.0	15.
150°–300°	40.2	38.3	38.8	38 8	25.0	25.0	36.8
+ 300°	37.	39.9	39.	47.2	75.	75.	48.2

of sulphur, nitrogen, and the different proportions in which they distil at different temperatures. There are also marked differences in iodine absorption, and in the coefficients of expansion. The latter were determined by ascertaining the specific gravity at 5°, 10°, 20°, and 25°, and dividing the differences in specific gravity at the different temperatures by five and multiplying the quotient by 100,000, the method described in Redwood's treatise on petroleum.

In the development of oil territory hitherto, no attempts have been made to ascertain the series of hydrocarbons which compose the main body of the crude oil. Beside the work of Pelouze and Cahours, Schoelemmer, and Warren on the Pennsylvania and Canadian oils, and the work carried on in this Laboratory, no attempts have been made to determine the form of the hydrocarbons in the lower distillates of American oils, and nothing whatever beside the unpublished work of this Laboratory on the determination of the composition of the portions with higher boiling points. Beside the work of Markownikoff on the Russian oils and the work of Warren and Storer on Rangoon petroleum, very little has been done in this direction on oils from other fields. On account of the ease in the preparation of commercial products from the lighter oils of Pennsylvania and Ohio, the ultimate composition was of less importance than it is now becoming in the development of oil fields that yield heavier crude oils, such as the oil territory in California, Texas, South America, Japan, and numerous other fields recently discovered. The methods that must be applied to these heavy oils are essentially different from the methods that have been universally in use since the beginning of the oil industry. In Japan, the promoters of those oil fields will have the advantage not only of all former experience in oil refining, but the further advantage of a knowledge of the hydrocarbons which form the main body of the crude oils. Japanese petroleum apparently differs from other heavy petroleums in that it contains smaller amounts of the benzol homologues. Benzol and its homologues were found in the Amaze oil, and some of the other crude oils, but fuming sulphuric acid failed to reduce materially the specific gravity of several of the distillates that should yield benzol hydrocarbons, if they were present.

Constituents of Petroleum from the Amaze Field.

The lightest oil from the Japanese fields is found in the Amaze territory. It consequently contains the largest proportion of more volatile

constituents. A combustion of Amaze crude oil gave 84.66 per cent carbon and 13.22 per cent hydrogen. After several distillations under a Hempel column, fractions collected in larger quantities at 68°, 98°, 119°, 135°, 62°, 96°, 216°. No attempts were made to ascertain the form of the hydrocarbons below 68°. The distillate collected at 68° gave as its specific gravity 0.7343, which indicated that hexane was not present in any considerable quantity. But nothing further was done toward identifying hexamethylene, which no doubt is the principal hydrocarbon in this distillate.

The distillate collected at 98°–100°, after purifying with fuming sulphuric acid, gave as its specific gravity at 20°, 0.7450.

A combustion gave the following percentages of carbon and hydrogen: —

0.1347 grm. of the oil gave 0.4221 grm. CO_2 and 0.1721 grm. H_2O.

	Calculated for C_7H_{12}.	Found.
C	85.70	85.45
H	14.30	14.20

Its index of refraction was found to be 1.4174, and the molecular refraction, 33.14; calculated for C_7H_{14}, 32.22. This hydrocarbon was therefore methylhexamethylene.

The distillate 118°–120°, after purification with fuming sulphuric acid, gave 0.7621 as its specific gravity at 20°. A combustion gave the following percentages of carbon and hydrogen: —

0.1406 grm. of the oil gave 0.4378 grm. CO_2 and 0.1812 grm. H_2O.

	Calculated for C_8H_{16}.	Found.
C	84.70	84.94
H	14.30	14.33

A determination of the index of refraction of this oil gave 1.4256, and the molecular refraction, 37.68; calculated for C_8H_{16}, 36.82. This hydrocarbon was therefore dimethylhexamethylene.

The distillate collected at 134°–135° was purified with fuming sulphuric acid and analyzed.

0.1528 grm. of the oil gave 0.4805 grm. CO_2 and 0.1950 grm. H_2O.

	Calculated C_9H_{18}.	Found.
C	85.70	85.76
H	14.30	14.29

It gave as its specific gravity at 20°, 0.7787.

The refractive index of this oil was found to be 1.4348, and the molecular refraction, 42.27; calculated for C_9H_{18}, 41.42. This constituent was therefore trimethylhexamethylene.

A distillate collected in considerable quantity at 160°–162°, which was purified with fuming sulphuric acid and analyzed: —

0.2055 grm. of the oil gave 0.6445 grm. CO_2 and 0.2556 grm. H_2O.

	Calculated for $C_{10}H_{20}$.	Found.
C	85.70	85.50
H	14.30	13.82

This oil gave as its specific gravity at 20°, 0.7902. Its index of refraction was 1.4418, and its molecular refraction, 46.94; calculated for $C_{10}H_{20}$, 46.03.

The distillate at 190°–192°, after purification with fuming sulphuric acid, gave as its specific gravity at 20°, 0.8061. Its composition was determined by analysis: —

0.1612 grm. of the oil gave 0.5046 grm. CO_2 and 0.2025 grm. H_2O.

	Calculated for $C_{11}H_{22}$.	Found.
C	85.70	85.35
H	14.30	13.96

The molecular weight of this hydrocarbon at the freezing point of benzol was 156; calculated for $C_{11}H_{22}$, 154. The index of refraction at 20° was 1.4482, and the molecular refraction 51.24; calculated for $C_{11}H_{22}$, 50.63.

The distillate 212°–214°, purified with fuming sulphuric acid, gave as its specific gravity at 20°, 0.8165. A combustion gave the following proportions of carbon and hydrogen: —

0.1875 grm. of the oil gave 0.5879 grm. CO_2 and 0.2451 grm. H_2O.

	Calculated for $C_{12}H_{24}$.	Found.
C	85.70	85.51
H	14.30	14.52

A determination of its molecular weight at the freezing point gave 172; calculated for $C_{12}H_{24}$, 168. Its index of refraction was 1.4535, and the molecular refraction, 55.76; calculated for $C_{12}H_{24}$, 55.23.

Composition of the Portions of Japanese Petroleum with High Boiling Points.

Japanese petroleum from different sources differs materially in its composition. From such oils as the Hirei no crystalline solids can be separated, even at low temperatures. But from others, such as the Amaze, Miyagawa, and Hiyama, crystalline solids separate from the higher fractions. The fraction 310°–315° atmospheric pressure, from Amaze crude oil became solid on cooling. The solid portion was separated by cooling and filtration; it was washed, pressed, and warmed with gasoline which removed all color. Melting point, 68°. The fractions above 225° were collected *in vacuo* under 30 mm. The purified solid from 225°–230° melted at 70°, that from 250°–275° at 73°, and that from 260°–265° at 74°. The solid from 225°–230° gave, by combustion, values showing it to belong to the series C_nH_{2n+2}.

0.1535 grm. of the oil gave 0.4890 grm. CO_2 and 0.1787 grm. H_2O.

	Calculated for $C_{12}H_{24}$.	C_nH_{2n}.	Found.
C	85.14	85.70	85.29
H	14.86	14.30	14.99

The fraction 250°–260°, 30 mm., from the Amaze oil gave the following percentages by combustion, also showing the series C_nH_{2n+2}: —

0.1654 grm. of the oil gave 0.5161 grm. CO_2 and 0.2233 grm. H_2O.

C	85.03
H	15.00

A combustion of the fraction 265°–270° gave values required for a hydrocarbon of the series C_nH_{2n+2}: —

0.1750 grm. of the oil gave 0.5469 grm. CO_2 and 0.2346 grm. H_2O.

C	85.21
H	14.81

In determining the molecular weight of this hydrocarbon at the boiling point of benzol, the following result was obtained: —

0.4190 grm. of the oil and 24.3 grms. benzol gave a rise in boiling point of 0.126.

Calculated for $C_{26}H_{54}$.	Found.
367	367

Determinations by the boiling point method of hydrocarbons with such high molecular weights are of necessity somewhat uncertain on account of the slight rise in boiling point. The question of the molecular weights of these solid hydrocarbons will receive more attention with the constituents of Pennsylvania and California petroleums with high boiling points.

The specific gravity of the solid 250°–260° is nearly the same as that of the corresponding hydrocarbon from Pennsylvania petroleum: —

	Japanese, 250°–260°, 30 mm.	Pennsylvania,* 292°–295°, 50 mm.
60		0.7977
70	0.7943	0.7950
80	0.7920	0.7943
90	0.7918	

The specific gravity of the Japanese solid at 60° could not be determined, because it was not liquid at that temperature.

Miyagawa Petroleum.

Although this oil is from a field situated only six miles from the Amaze field, it differs essentially in its specific gravity, and in the proportions in which it distils, from the Amaze oil. The crude oil was distilled under atmospheric pressure, and the distillation of the lower portions continued until they came together in larger quantities at temperatures at which distillates were collected from the other oils. The specific gravity of the distillates after treating with concentrated sulphuric acid is as follows: —

98°–100°.	118°–120°.	134°–136°.	160°–162°.	194°–196°.	212°–214°.	228°–230°.
0.7364	0.7631	0.7772	0.8088	0.8493	0.8674	0.8770

The last three fractions were also treated with fuming sulphuric acid and the specific gravity determined: —

194°–196°.	212°–214°.	228°–230°.
0.8412	0.8650	0.8720

The slight change after the thorough treatment with fuming sulphuric acid shows that no benzol homologues were present in these portions, yet the specific gravity of the hydrocarbons above 196° is considerably higher than of those from Amaze oil or from Hirei oil. The distillates

* Unpublished data.

collected under atmospheric pressure were thoroughly treated with fuming sulphuric acid, washed, dried, and their molecular refraction determined: —

Distillate.	Refractive Index.	Molecular Refraction.	
		Calculated.	Required.
98°–100°	1.4117	33.14	32.21
118°–120°	1.4163	36.92	36.82
134°–136°	1.4261	41.51	41.42
160°–162°	1.4463	46.26	46.03
194°–196°	1.4605	50.27	50.63
214°–216°	1.4706	54.34	55.23

Hirei Petroleum.

A combustion of Hirei crude oil gave 82.28 per cent of carbon and 13.19 per cent of hydrogen. In the distillation of the Hirei oil, fractions collected within the same limits of temperature as those from the other crude oils. The distillate collecting in the vicinity of 98°, after treatment with sulphuric acid, gave 0.7412 as its specific gravity. Its molecular weight at the freezing point of benzol was 98; required for C_7H_{14}, 98. Its index of refraction was 1.4095, and its molecular refraction, 32.77; required for C_7H_{14}, 32.22.

The fraction 118°–120° gave as its specific gravity 0.7523. Its molecular weight was 114; required for C_8H_{16}, 112. Its index of refraction was 1.4151, and its molecular refraction, 37.34; required for C_8H_{16}, 36.82.

The fraction at 135° gave as its specific gravity 0.7676. Its molecular weight was 128; required for C_9H_{18}, 126. Its index of refraction was 1.4372, and its molecular refraction, 42.12; required for C_9H_{18}, 41.42.

The fraction 162° gave for its specific gravity 0.7887. Its molecular weight was found to be 137; required for $C_{10}H_{20}$, 140. Its index of refraction was 1.4372, and its molecular refraction, 46.60; required for $C_{10}H_{20}$, 46.03.

The specific gravity of the fraction at 196° was 0.8192. Its index of

refraction was 1.4516, and its molecular refraction, 50.78; required for $C_{11}H_{22}$, 50.63.

The specific gravity of the fraction 216° was 0.8327, and the molecular weight, 172; required for $C_{12}H_{24}$, 168. Its index of refraction was 1.4599, and its molecular refraction, 55.22; required for $C_{12}H_{24}$, 55.23.

The specific gravity of these distillates from Hirei oil is somewhat higher than was found in the corresponding distillates from Amaze oil, and the differences increase with increasing molecular weights. It was at first thought that this was due to incomplete removal of benzol hydrocarbons, but still further treatment with fuming sulphuric acid failed to diminish these values. It is probable that the oil contains hydrocarbons with more than one methylene ring.

The results of this examination show that Japanese petroleum is composed for the greater part of hydrocarbons of the series C_nH_{2n}, — the methylene hydrocarbons. Probably the very heavy oils contain hydrocarbons with two or more methylene rings, of the series C_nH_{2n-2} or C_nH_{2n-4}. Some of the oils contain solid paraffine hydrocarbons, others do not. The proportion of benzol derivatives in the oils examined is relatively much smaller than in California petroleum. The proportion of nitrogen compounds and of sulphur compounds is quite variable. In some of the oils the percentages were nearly as large as any found in California petroleum, in others the amounts were much smaller.

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THE ECLIPSE CYCLONE AND THE DIURNAL CYCLONES.

Results of Meteorological Observations in the Solar Eclipse of May 28, 1900.

By H. Helm Clayton.

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Presented November 14, 1900. Received December 12, 1900.

The path of total solar eclipse in the United States on May 28, 1900, was visited by a number of experts and trained observers, who took meteorological observations as a part of the program on the day of the eclipse. These included Mr. A. Lawrence Rotch and Mr. S. P. Fergusson at Washington, Ga.; Mr. O. B. Cole at Centerville, Va.; Mr. G. W. Pickard at Virginia Beach, Va.; and myself at Wadesboro, N. C. These observations were sent to the Blue Hill Meteorological Observatory and given to me for discussion. Besides these I obtained records from a number of well-equipped observatories in North America. These included the Toronto Observatory, the New York Central Park Observatory, the Blue Hill Observatory, the Belen College Observatory of Havana, the McGill College Observatory of Montreal, the Meteorological Station at Cornell University, the City Engineer's Office at Providence, R. I., and observations by Mr. Eddy at Bayonne, N. J. These observations were all within the area of partial eclipse, and the data were furnished by the kindness of the directors.

The details of the discussion of the observations are published in a Bulletin of the Blue Hill Meteorological Observatory.* The results embody certain conclusions of general interest which I am permitted to present to the Academy.

The meteorological changes due to the eclipse were separated from other changes of greater length, such as the diurnal and cyclonic, by interpolating a uniform change between the beginning and the end of the eclipse and subtracting this from the observations. For example, in Figure 1 is plotted the observations of temperature at Wadesboro, N. C.

* Annals of the Astron. Observatory of Harvard College, XLIII. No. 1.

The outside vertical lines B and E show the beginning and end of partial eclipse, and the central vertical lines T show the times of total eclipse. The dotted straight line connects the observed temperature at the begin-

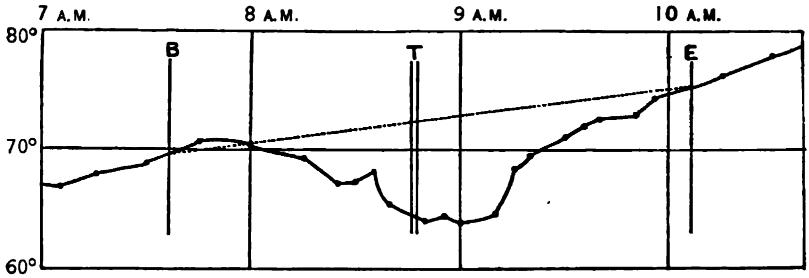


FIGURE 1.

ning and end of the eclipse, and represents the interpolated uniform change. The observed temperatures are shown by the unbroken curved line, and the departures of these from the values represented by the dotted line is assumed to be the depression of temperature arising from the eclipse. The pressure, humidity, and vapor tension were treated in the same manner.

In order to obtain the eclipse wind in velocity and direction, the observations were treated in the following manner.

In the accompanying diagram, Figure 2, let A B represent the direction and velocity of the wind prevailing independent of the eclipse, and

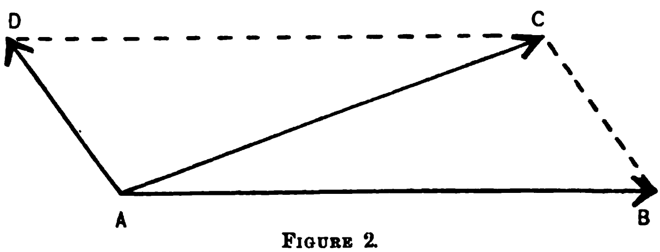


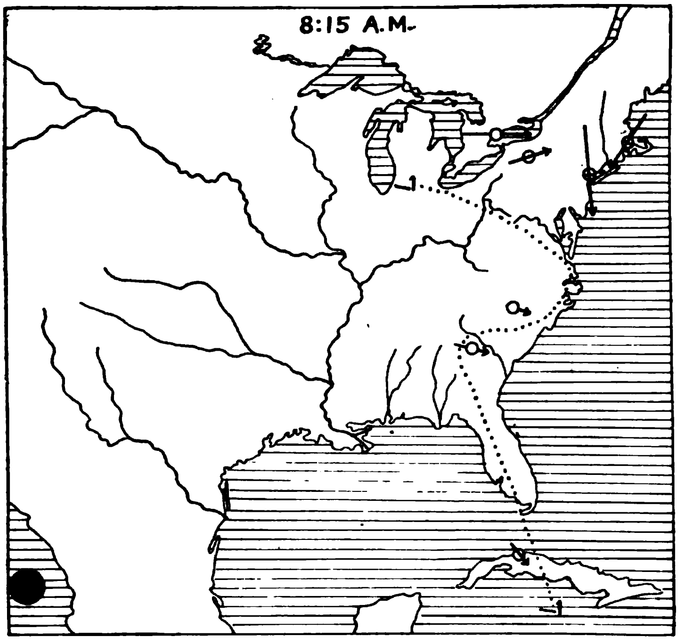
FIGURE 2.

A C the wind observed at any moment during the eclipse; then completing the parallelogram of forces, A D will represent the eclipse wind in direction and velocity. The prevailing wind was derived from the mean of the winds immediately preceding and following the penumbra, or, what was found to be practically the same thing, from the mean wind direction during the passage of the penumbra, since the eclipse wind was

from opposite directions during this time. The penumbra is used to indicate the area of partial eclipse, and the umbra to indicate the area of total eclipse. The mean wind and the eclipse wind were at first determined graphically for all the stations; then as the results seemed to be of importance, they were rigidly computed for all the stations where the observations were sufficiently accurate to warrant it. These results, when plotted, indicate very clearly an outflow of wind from around the umbra, and an inflow around the borders of the penumbra.

But there are certain irregularities due to the normal irregularities of the wind. In order to diminish the effect of these, I smoothed the observations by the formula $\frac{a + 2b + c}{4}$. These winds were plotted at their proper places on maps of the United States for 8.15 A.M., 75th meridian time, when the umbra was about to enter the American continent from the Pacific, and also plotted for 9 A.M., when the umbra had passed off the coast of the United States on to the Atlantic. These maps are shown in Figure 3. The position of the umbra is shown on each map by a dark circular area. The depressions of temperature by the eclipse are shown by numerals on the maps, and isotherms are shown by dotted lines. The weather conditions are indicated by symbols, and the direction and velocity of the eclipse wind are indicated by the direction and length of the arrows. The winds were practically reversed in direction as the umbra moved from one side of the continent to the other, but both charts show a distinct anticyclonic circulation and an outflow of air extending from the umbra, or central area of the eclipse, to a distance of about fifteen hundred or two thousand miles. In the 8.15 A.M. chart the outer limit of the outflow appears to be in New York, beyond which there is an inflow. In this chart the stations of observations are so far in advance of the central area of the eclipse that no appreciable depression of temperature is shown; but in the 9 A.M. chart, which coincides with the greatest depression of temperature at Wadesboro, Washington, and Virginia Beach, there is a central area shown by the isotherms where the depression of temperature exceeds 8° F. This area of greatest cold lags behind the umbra about five hundred miles.

The charts in Figure 3 show only a portion of the eclipse area, or penumbra, which was about five thousand miles in diameter. Hence the charts do not give an idea of the winds on the outer area of the penumbra, or the successive changes which occurred at any one station as the eclipse passed over it. A view of these changes is obtained by plotting the winds, temperature, etc., at given stations when they were successively



OCLEAR; ⊖FAIR; ⊕CLOUDY.

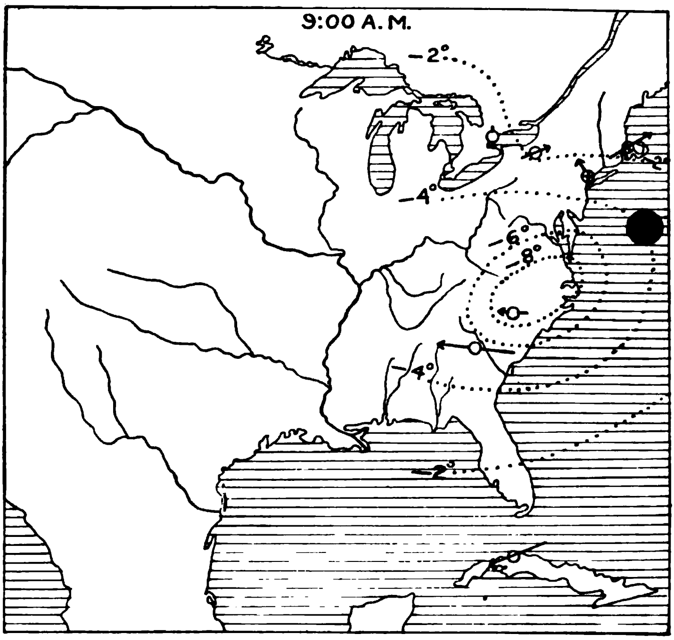


FIGURE 3.

in different portions of the eclipse area. The eclipse shadow travelled with a velocity somewhat greater than two thousand miles an hour. By placing the stations at their proper distances from the path of the umbra and plotting the successive fifteen minute observations at intervals of about five hundred miles, a synoptic chart is obtained showing the conditions observed at any given station or group of stations when they were in different portions of the eclipse area. In this way Figure 4 was constructed. In this diagram the direction and width of the path of the umbra is

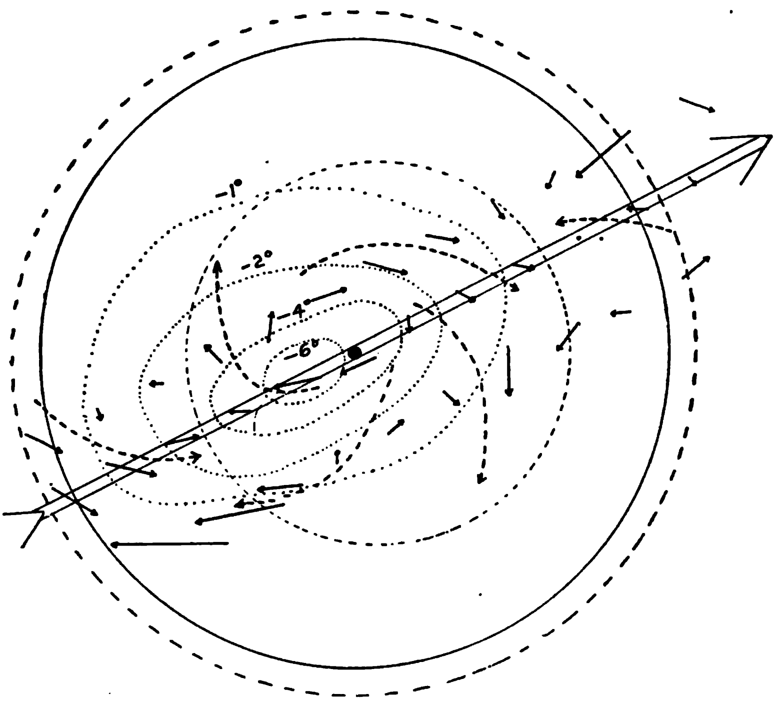


FIGURE 4.

shown by parallel lines forming a long arrow. The central shaded area shows the umbra, and the outer unbroken circle shows the outer limit of the penumbra. The data north of the path of the umbra are derived from the mean of the observations at Ithaca, Toronto, and Blue Hill; the data along the path are derived from the mean of observations at Washington, Ga., and Wadesboro, N. C.; the data south of the path are from Havana.

Figure 4 indicates distinctly an anticyclonic circulation of the wind around the centre of the eclipse extending out to a distance of about fifteen hundred miles from the umbra. Outside this area there is an equally distinct cyclonic circulation about one thousand miles in width extending out to and beyond the edge of the penumbra. Beyond this there are indications of another ring of outflowing winds. The inner circle of broken lines in the diagram represents a probable ring of low-air pressure. The outer circle of broken lines surrounding the penumbra represents a probable ring of high pressure. The isotherms are shown by dotted lines. They show an elliptical area of cold air central about five hundred miles in the rear of the umbra. The greatest depression of temperature is north of the track of the umbra. This was chiefly due to the continental effect. The difference may also have been due in part to the fact that the sky was partly cloudy at Havana. On comparing stations similarly situated as regards the eclipse, it was found that the depression of temperature due to the eclipse was less at stations where it was cloudy, and that it also diminished with height above the sea. This indicates that the cooling is chiefly in a thin stratum of air very near the earth's surface. The analogy to the diurnal change of temperature would also indicate that this must be true. The shape and position of the areas showing the humidity departures are so similar to those of temperature that it is not deemed necessary to reproduce them. The chief difference is that in one case the departures are plus and in the other minus. In other words, during the eclipse there is a rise of absolute and relative humidity and a fall of temperature.

The observations indicate very clearly a lowering of the air pressure during the eclipse, the minimum of pressure occurring soon after the minimum of air temperature. This is shown by records made at Washington, Ga., at Toronto, and at Blue Hill. The accompanying diagram

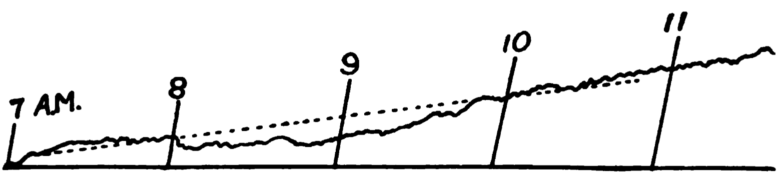


FIGURE 5.

shows a record made by an "aerograph," or air barometer, at Toronto. This barograph, devised by F. Napier Denison, has its air-chamber buried eight feet below the surface of the ground to protect it from

external changes of temperature. The curve is traced from the record, and is given on the same scale without correction in any way. The eclipse began at Toronto about 7.47 A.M. and ended about 10.18 A.M. A straight dotted line is drawn through the curve connecting the pressure recorded at the beginning and end of the eclipse. It is seen that the pressure was generally below the dotted line throughout the eclipse, but there was an upward swell between 8 and 9 A.M., shortly preceding the middle of the eclipse. Immediately preceding and following the beginning and end of the eclipse the curve rises above the dotted line, indicating a ring of high pressure surrounding the umbra, and thus agreeing perfectly with the distribution of pressure demanded by the wind circulation. I find that when the changes of pressure observed during previous eclipses are separated from the normal diurnal changes, they show changes very similar to those given by the curve for Toronto, except that the rise in pressure near the middle of the eclipse is greater for stations in the path of total eclipse. This central rise of pressure is due to the increased density of the air from cold, and on it depends the outflow of air surrounding the umbra. Hence in normal eclipses there is a central area of relatively high pressure; surrounding this is a ring of minimum pressure, and beyond this, outside the edge of the penumbra, is a ring of maximum pressure.

The low temperature, the circulation of the winds, and the form of the pressure curve accompanying the eclipse of May 28, 1900, all proclaim the development by the eclipse of a cold-air cyclone, the theory of which has been so well worked out by Ferrel that no better description of it could be given than in his own words. Ferrel maintains from theoretical considerations that cyclones necessarily have an inner area of low pressure, surrounded by a ring of high pressure, which Professor Davis has named a *pericyclone*. Ferrel further maintains that a cyclone may have its origin either in a high temperature increasing toward a central area, or in a low temperature decreasing toward a central area. The one he calls a cyclone with a warm centre, the other a cyclone with a cold centre. Of cyclones with a cold centre he says: —

"If for any reason the central part of any given portion of the atmosphere of a somewhat circular form is maintained in any way at a lower temperature than the surrounding parts, and the temperature gradient on all sides is somewhat symmetrical, we have approximately the conditions which give rise to a cyclone. In this case it is readily seen that there must be a vertical circulation, as in the ordinary cyclone, but that it is reversed, out from the centre below, and in toward the centre above,

with a gradual settling down of the air in the interior to supply the outward current beneath. This vertical circulation, as in the case of the ordinary cyclone, gives rise to a cyclonic motion in the interior and an anticyclonic in the exterior part of the air under consideration, but in this case the gyratory velocity is greatest above and is less at lower altitudes, diminishing down to the earth's surface, where it is least. In the anticyclonic part the reverse takes place, the gyratory velocity being least above and greatest down near the earth's surface. The distance from the centre at which the gyratory velocity vanishes and changes sign, is greatest above and gradually becomes less, with decrease of altitude down to the earth's surface, where it is nearest the centre. . . . The conditions of a cyclone with a cold centre which are the most nearly perfect are those furnished by each hemisphere of the globe, as divided by the equator, in which the pole is the cold centre, and the temperature gradient from the pole toward the equator is somewhat symmetrical in all directions from the centre. . . . The easterly motions in the higher latitudes and the westerly ones in the lower latitudes, in the one case, correspond to the cyclonic in the interior and the anticyclonic in the exterior part, and the belt of high pressure near the tropics to that of high pressure in the case of any cyclone with a cold centre. . . . The centre of a cyclone with a cold centre may or may not have a minimum pressure, according to circumstances. A certain amount of temperature gradient, and of pressure gradient which is independent of the gyratory motion, as explained in the case of the general circulation of the atmosphere, is necessary to overcome the friction in the lower strata and to keep up the vertical circulation, upon which the cyclone depends; and the pressure gradient, which depends upon the temperature gradient and is independent of the gyrations, may be such that the increase of pressure in the central part due to this cause may be greater than the decrease of pressure arising from the cyclonic gyrations, especially where surface friction is great." *

The eclipse cyclone is of especial interest from a theoretical point of view, because its origin, clearly connected with the fall of air temperature attending the eclipse, is freed from all questions of condensation of vapor or of the dynamic effects due to the meeting of air currents whose possible influence complicates the question as to the origin of the ordinary cyclone. The eclipse may be compared to an experiment by Nature in which all the causes that complicate the origin of the ordinary

* A Popular Treatise on the Winds, pp. 337–339.

cyclone are eliminated except that of a direct and rapid change of temperature. The results derived from the observations by eliminating the influence of other known phenomena give quantitatively the effects of a given fall of temperature near the earth's surface in a given time. They show that a fall of temperature is capable of developing a cold-air cyclone in an astonishingly short time, with all the peculiar circulation of winds and distribution of pressure which constitute such a cyclone. They show, furthermore, that a fall of temperature of the air does not act primarily to cause an anticyclone but a cyclone, and the anticyclone is a secondary phenomenon, or rather a part of the cyclone.

The eclipse cyclone shows no apparent lag or dynamic effect due to the inertia of the air. To keep pace with the eclipse shadow moving about two thousand miles an hour the eclipse cyclone must continuously have formed within the shadow and must have dissipated in the rear almost instantly. In this way its motion may be considered to have a certain analogy to wave motion. Any given particle of air moving with the velocity of the eclipse winds could not have moved more than five miles as a maximum during the passage of the eclipse. Hence all the changes of pressure must have been derived from the deflective influence of the earth's rotation acting on air moving this distance.

In brief, the meteorological effects of the eclipse are important —

(1) Because they confirm so fully Ferrel's theory of the cold-air cyclone;

(2) Because they show the wonderful rapidity with which cyclonic phenomena can develop and dissipate in the atmosphere; and

(3) Because they show that cyclones do not necessarily drift with the atmosphere, but move with their originating cause, which in the eclipse had a progressive velocity of about two thousand miles an hour.

The Diurnal Cyclones.

The discovery that the brief fall of temperature attending a solar eclipse produces a well-developed cyclone which accompanies the eclipse shadow at the rate of about two thousand miles an hour, suggests that the fall of temperature due to the occurrence of night must also produce or tend to produce a cold-air cyclone. Since the heat of day produces or tends to produce a warm-air cyclone, there must tend to occur each day two minima of pressure, one near the coldest part of the day, and another near the warmest part of the day, with areas of high pressure between them due to the overlapping of the pericyclones surrounding the

cold-air and the warm-air cyclones respectively. These causes must produce entirely or in part the well-known double diurnal period in air pressure. At any rate, in view of the fact that an eclipse causes a cyclone over half a hemisphere, it will be necessary before rejecting such a theory to show that the fall of temperature at night does not produce a cyclone, or that this cyclone and the corresponding warm-air cyclone of the day do not appreciably influence the barometer.

The points in favor of the theory that the double diurnal period in pressure is due to two diurnal cyclones, one developed by the cold of night and the other by the heat of day, may be stated in brief as follows. The theory is based on well-known physical laws. The possibility of a cold-air cyclone under conditions similar to the diurnal cyclone is confirmed by the eclipse cyclone. The theory explains the annual oscillation of the time of maxima and minima of pressure in the diurnal period; and explains the occurrence of a third maximum in high northern latitudes in winter. The theory also explains why the warm-air cyclone is well developed over continents, and on clear days, and causes a marked fall in the barometer during the afternoon, while the morning minimum of pressure over continents does not attain an excessive development as compared with that over oceans where there is slight retardation of the air movements on which the fall of the barometer in the cold-air cyclone depends.

The diurnal cyclones move from east to west, contrary to the motion of ordinary cyclones in temperate latitudes. Their velocity of motion is about one thousand miles an hour at the equator, and diminishes toward the poles. The two charts in Figure 6 indicate the circulation of the surface winds and upper currents in the diurnal cyclones. In these charts the ordinates represent the hours of the day, and the abscissas represent distances from the equator. The data for the surface winds are derived from observations at Blue Hill, lat. 42° 13′ N., long. 71° 7′ W., and Cordoba, Argentina, lat. 31° 25′ S., long. 64° 12′ W.* The directions of the arrows represent in the usual way wind directions, and the position of the arrow shows the time of maximum frequency of each wind. Thus the greatest diurnal frequency of southerly winds occurs at Cordoba at 7 A.M., and at Blue Hill between 7 and 8 P.M. There is also a second maximum frequency of southerly winds at Blue Hill about 10 A.M. The wind arrows at Cordoba and Blue Hill are, in general,

* Annals of the Astron. Observatory of Harvard College, XXX. Pt. iv., 415 and 419.

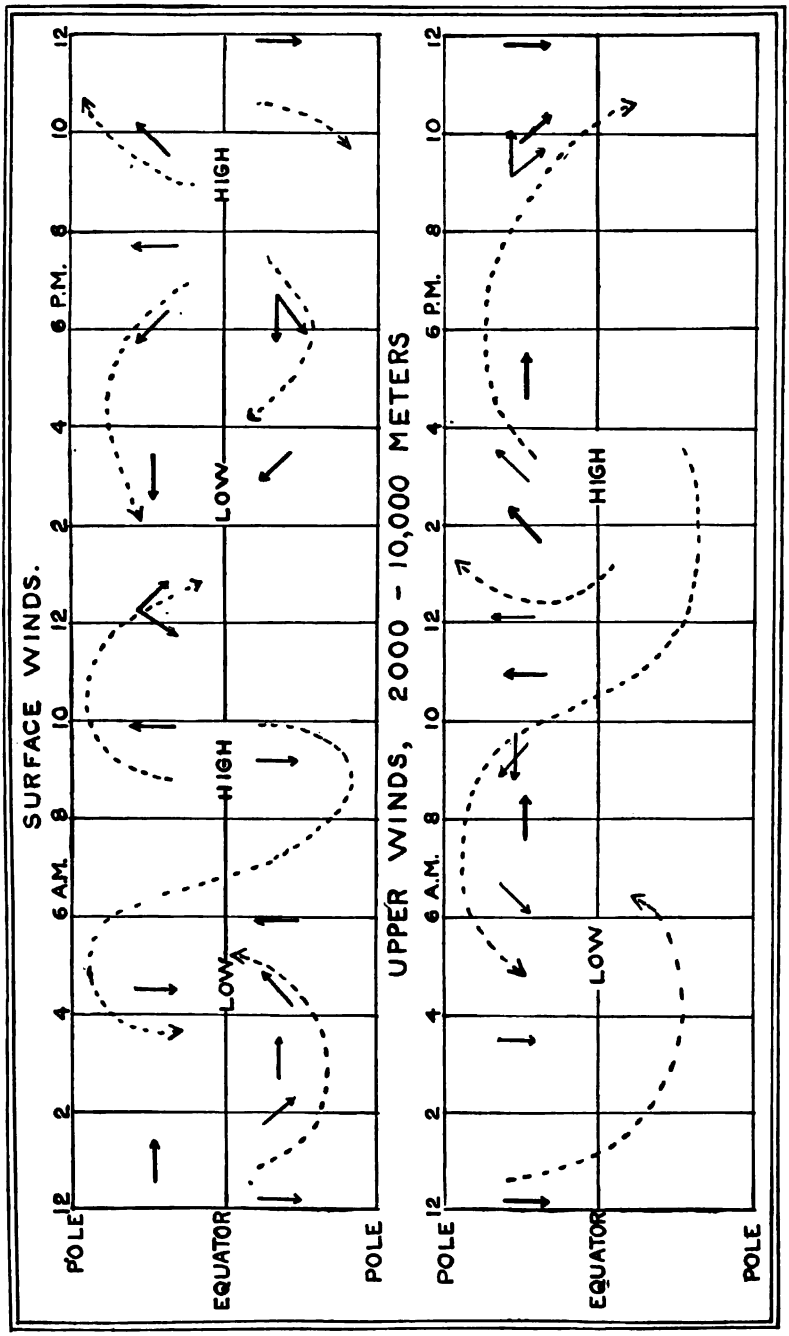

SURFACE WINDS.
12 2 4 6 A.M. 8 10 12 2 4 6 P.M. 8 10 12
HIGH
LOW
HIGH
LOW
POLE
EQUATOR
POLE
UPPER WINDS, 2000 - 10,000 METERS
12 2 4 6 A.M. 8 10 12 2 4 6 P.M. 8 10 12
HIGH
LOW
POLE
EQUATOR
POLE

Figure 6.

in opposite directions, and distinctly indicate a circulation of the wind around two cyclonic centres passing along the equator, and an outflow from high pressures half-way between them. The lower chart, headed "Upper Winds," shows the hours of greatest frequency of each wind direction in the upper air between 2,500 and 10,000 meters. These times were determined by observations of clouds at Blue Hill, and from hourly wind records on the Säntis in Switzerland. Cloud strata at three different levels between 3,000 and 10,000 meters above Blue Hill each gave a result similar to the other. This is indicated by heavy arrows in the chart.* The observations on the Säntis at an elevation of 2,500 meters are indicated by the light arrows in the same diagram. There are no observations available at these heights south of the equator, but the observations north of the equator indicate a circulation very different from that at the earth's surface. There is apparent at this height only one cyclonic and one anticyclonic circulation. The low pressure in the cold-air cyclone of night persists at these levels, and probably with increased intensity, while the low pressure in the warm-air cyclone of day has been replaced by a high pressure and an anticyclonic circulation.

* Annals of the Astron. Observatory of Harvard College, XXX. Pt. iv., 415 and 419.

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CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

L. — *AN APPARATUS FOR RECORDING ALTERNATING CURRENT WAVES.*

BY FRANK A. LAWS.

WITH A PLATE.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF THE ASSACHUSETTS INSTITUTE OF TECHNOLOGY.

L. — AN APPARATUS FOR RECORDING ALTERNATING CURRENT WAVES.

BY FRANK A. LAWS.

Presented May 10, 1900. Received December 15, 1900.

THE apparatus forming the subject of this communication was constructed at the Rogers Laboratory in 1898, and has proved of sufficient value to merit a short description. In brief, the arrangement gives us a modification of the "contact method," by which the record is rendered continuous and traced photographically.

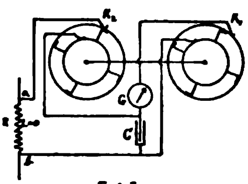

FIG I

The necessary electrical connections are shown in the diagram. K_1 and K_2 are two rigidly connected contact wheels of ebonite. Into the periphery of each wheel are set four brass blocks. These are accurately placed 90° apart. Upon each wheel a brush and collector ring give permanent contact with the blocks. Another brush resting on the periphery of the wheel completes electrical connection as the blocks pass under it. The brushes are so placed that contact is made and broken at K_2 before K_1 closes. The contact wheels are driven by a synchronous motor, which gives one revolution for four complete alternations of the E.M.F. G is a dead-beat galvanometer, and C is an adjustable condenser. The leads a and b are carried to the points between which the P.D. is to be investigated. By inspection of the diagram it will be seen that once on each wave and at a definite point the condenser C is charged to the potential existing between a and b. As the charge is determined by the breaking of the contact, the blocks may be of sufficient width to eliminate the effect of the jumping of the brushes. Also the resistance at the contact will not be of sufficient magnitude to prevent complete charging of the condenser.

The function of K_1 is to discharge the condenser through the galvanometer after K_2 has broken circuit. The instrument would ordinarily experience a constant deflection, but K_1 and K_2 are rigidly connected and mounted on a radial arm, which is geared to the shaft so that it moves very slowly. The effect is to gradually move the contact point over the wave. The deflection of the galvanometer will at any instant be proportional to the P.D. between *a* and *b* at the instant of breaking at K_2, or in other words, the deflection follows the wave form.

The actual arrangement is shown in Figure 2 (see Plate), where the contact device, the synchronous motor, and the direct current motor used for starting the apparatus will be seen. By use of worm gearing the wheel train necessary for moving the brushes is made very compact; the reduction for the instrument shown is 7200 to 1.

I have found Sullivan's Universal Galvanometer to be a most satisfactory instrument for use with the apparatus. This galvanometer, of the D'Arsonval type, has a carefully balanced coil, so that it is not very susceptible to mechanical disturbances; also the magnetic damping is most carefully adjusted. The instrument is not of great sensitiveness, but owing to the stiff suspension the zero is perfectly definite.

The camera used for recording the curves is shown in Figure 3 (see Plate). The plate is contained in an ordinary plate holder. This is moved vertically by a fine wire which is wound on a drum, seen in Figure 2, just in front of the lower worm-wheel. This drum can be thrown in at pleasure by a pin clutch. The slide of the plate holder is held stationary by a pin, so that the plate is exposed as the holder is drawn up.

The front of the camera, shown removed, is provided with a narrow slit about $\frac{1}{100}$ of an inch wide. In front of it are projecting lips 9 inches long and $\frac{1}{8}$ of an inch apart. They are blackened within and serve effectually to shut out extraneous light, and thus prevent fogging of the plate. The spot of light used was the sharply focussed image of the filament of an incandescent lamp. An alternative arrangement is to use a plate of ground glass in the holder, and to have a straight-edge fastened across the guides. It is then easy to keep the point of a pencil in contact with it and upon the spot of light.

The arrangement described is of course a device for obtaining the average wave, and unsuitable for recording transient phenomena. The time taken in recording a wave at 120 cycles per second is about $1\frac{1}{2}$ minutes.

The adjustable condenser allows one to adapt the apparatus to varying conditions, so the E.M.F. curves may be taken directly, and the

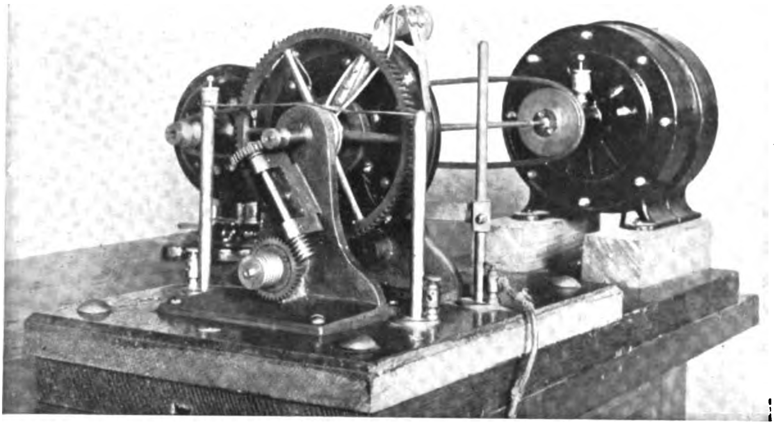

Figure 2.

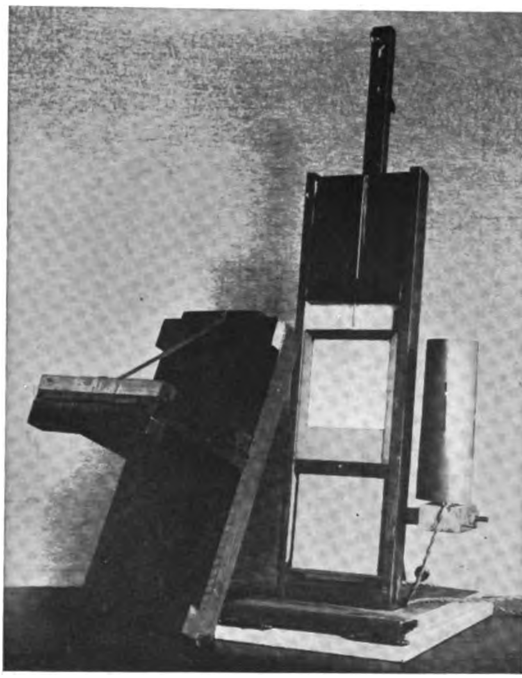

Figure 3.

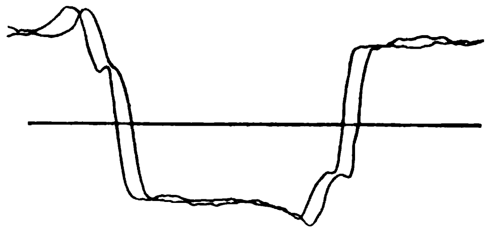

FIGURE 4. — Potential difference between the carbons of an enclosed arc, in series with reactive coil.

The curves were taken about one minute apart with a view to testing the concordance of the readings.

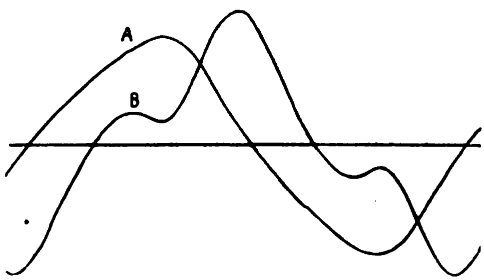

FIGURE 5. — *A*, potential difference between the terminals of a small alternating current motor. *B*, current through motor.

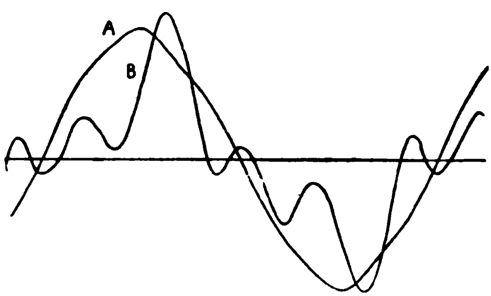

FIGURE 6. — Curve *A* is E.M.F., and *B* is current in one phase of a quarter-phase synchronous motor running idle with the field adjusted for minimum current. Source of power was a three-phase dynamo with phasing transformers arranged on the Scott system.

current curves by the use of a drop wire, as indicated in Figure 1. In starting the arrangement it is very easy to determine when the proper

speed for synchronism has been attained by watching the spot of light, or by listening to a telephone which is inserted in place of the galvanometer. With the latter one hears slow beats as the contact moves over the wave. Opposite are given some examples of the records obtained with the device.

Rogers Laboratory of Physics,
June, 1900.

Proceedings of the American Academy of Arts and Sciences.

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SUGGESTION CONCERNING THE NOMENCLATURE OF HEAT CAPACITY.

BY THEODORE WILLIAM RICHARDS.

SUGGESTION CONCERNING THE NOMENCLATURE OF HEAT CAPACITY.

By Theodore William Richards.

Received December 19, 1900. Presented January 9, 1901.

The word "calorie" has come to have so many significations as to have lost definite meaning, unless qualified by an explanatory phrase. For this unfortunate condition of affairs, which is due primarily to the variability of the specific heat of water, the best remedy seems to me to be the general use of a new standard for the measurement of heat capacity.

The growing tendency to refer all energy measurements to the centimeter-gram-second basis makes it fitting that heat also should be measured directly in these terms. It is not unusual to do this, as far as heat-energy is concerned; but the practice is hampered by the fact that the standards of temperature and heat-capacity have no rational relation to the so-called absolute units. One calorie equals about 42,000,000 ergs, or 4.2 joules. Would it not be a convenience to arrange the standards of heat measurement so that the direct product of heat capacity and change of temperature would be expressed in joules? Nearly ten years ago Ostwald pointed out some of the advantages of such a practice,* but the suggestion does not seem to have received the attention which it deserves.

One way to accomplish the desired result would be to construct a new scale of temperature with degrees about $\frac{10}{42}$ the size of the present centigrade degrees, and to retain the specific heat of water at a definite temperature as the unit of capacity. This course retains one of the disadvantages of our present system, and is open to several other objections, the chief of which would be the variability of the degree with each new measurement of the value of the mechanical equivalent.

Another obvious course is to retain the centigrade degree, measured by the hydrogen or helium thermometer, as final, and to choose for the unit of capacity that capacity which is warmed 1 degree centigrade by

* Zeitschr. phys. Chem., 9, 577 (1892).

1 joule (1 watt-second, or 10^7 ergs). Here the unit of capacity will vary with each new increase in accuracy in the determination of the mechanical equivalent; but capacity is a less tangible dimension than temperature, and its variation would cause less instrumental confusion.

This convenient unit of capacity would be nearly represented by the heat capacity of a gram of magnesium at low temperatures (—50°), or that of a gram of aluminum at high temperatures (about 290° C.). At ordinary temperatures an alloy of zinc and magnesium containing about 5.5 per cent of zinc would probably have the desired capacity.

Specific heats are frequently spoken of in terms of *calories*, thus confounding heat capacity with energy. As a matter of fact, the idea of specific heat is mathematically nothing but a simple ratio like specific gravity, — a pure number without physical dimensions. The unit suggested here is rather to be compared with *density*; it has the definite dimension of energy divided by temperature.

It seems to me that a name for this unit would greatly assist the beginner to discriminate between energy and capacity. Would not the name "mayer," in honor of the unfortunate Julius Robert Mayer, one of the discoverers of the first law of energy, be a convenient and fitting term for the centimeter-gram-second ÷ centigrade unit of heat capacity?

On this basis the heat capacity of a gram of water at twenty degrees centigrade is about 4.181 mayers, and that of a gram of liquid mercury is $.0333 \times 4.18 = 0.139$ mayers. The gas constant becomes 8.32 mayers, if the atomic weight of oxygen is taken as 16; and the Dulong and Petit constant or gram-atomic heat capacity becomes about 26.5 mayers on the same basis. These numbers are all of convenient magnitude. For larger values, such as the heat capacities of solutions used in thermochemistry, the kilomayer is a convenient unit. For instance, the capacity of $HCl + 100\ H_2O$ is 7.41 kilomayers, while that of a similarly dilute solution of 40 grams (a mol) of sodic hydroxide is 7.42 kilomayers. The solution produced by mixing these two has a capacity of 15.02 kilomayers. In order to show how convenient these figures are as a basis of calculation, it is only necessary to point out that this difference of 0.19 kilomayer between the capacities of factors and product indicates that the heat of neutralization will vary 0.19 kilojoule* for each degree of tem-

* Ostwald has pointed out the convenience of the *kilojoule* as a unit in thermochemistry, in the latest edition of the "Grundriss der allgemeinen Chemie." It seems to me that it would be well to represent this useful unit by kj., in analogy to km. and kg., rather than by J., which might be mistaken as an abbreviation for joule. Kilomayer may be abbreviated to kmy.

perature, according to the well-known equation $C_T - C_T = \frac{U_{T'} - U_T}{T' - T}$, where capacities are represented by C, heats of reaction by U, and temperatures by T.

Since entropy has the dimensions of heat capacity, it too may be measured in mayers. This application of the new name may lend concreteness to an idea which has been to some a stumbling-block.

The greatest gain to be derived from the consistent use of the "absolute" unit of heat capacity is to be found in the field of electrochemistry. Here even technical men have used for several years the admirable system of units resting upon the centimeter-gram-second basis. The increasing use of both the thermodynamic and osmotic equations of electrochemistry will make the ready application of these units to heat and gas energy almost a necessity.

Cambridge, Mass., October 31, 1900.

Proceedings of the American Academy of Arts and Sciences.

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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY
OF HARVARD COLLEGE.

SYMMETRICAL TRIIODBENZOL.

BY C. LORING JACKSON AND G. E. BEHR.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

SYMMETRICAL TRIIODBENZOL.

By C. Loring Jackson and G. E. Behr.

Presented December 12, 1900. Received December 20, 1900.

So far as we can find, three triiodbenzols have been described in the chemical literature, but the constitution of only one has been established thoroughly; this is the unsymmetrical (1 . 2 . 4) isomere melting at 76° obtained by Kekulé * from the action of iodine and iodic acid on benzol. More recently Hantzsch † has also made it from the diioddiazobenzol iodide prepared from diiodaniline and found that it melts at 77°.

The other two isomeric triiodbenzols were made by Istrati and Georgescu ‡ by heating together benzol iodine and concentrated sulphuric acid. Unfortunately their original paper is not at our disposal, so that we know their work only from the abstracts of it in the "Jahresbericht über die Fortschritte der Chemie" and Beilstein's Handbuch (third edition). From these it appears that they ascribed the unsymmetrical constitution (1 . 2 . 4) to their compound melting at 85°, and the adjacent structure (1 . 2 . 3) to that melting at 182° to 184°, but there is no statement that they determined these constitutions experimentally. The experiments of Kekulé and Hantzsch just cited prove that the unsymmetrical isomere melts at 77° (or 76°), and, therefore, their compound melting at 85° cannot have this structure.

Under these circumstances it seemed worth while to prepare the symmetrical triiodbenzol and to prove its constitution by experiment; accordingly we made the triiodaniline by the method of Michael and Norton, § that is, treating chloride of aniline with monochloride of iodine; and replaced the amido group in this body by hydrogen by means of the diazo reaction.

* Ann. Chem. (Liebig), CXXXVII. 164 (1866).

† Ber. d. chem. Ges., XXVIII. 684 (1895).

‡ Buletinul d. Soc. d. Sciinte Fiz. d. Bucuresci, I. 62. Jarhresb. Chem. 1892, 1063. Beilstein's Handbuch (3d Edition), III. 78.

§ Ber. d. chem. Ges., XI. 111 (1878).

The triiodbenzol thus obtained melted at 181°, which suggested that it was identical with the substance made by Istrati and Georgescu melting at 182° to 184°, and this was proved to be the case by treating it with fuming nitric acid, which converted it into a triioddinitrobenzol melting at 210°, whereas Istrati and Georgescu * under similar conditions obtained from their substance a dinitro derivative melting at 210°–212°. That our triiodbenzol had the symmetrical constitution (1 . 3 . 5) was very probable, because the trichloraniline and the tribromaniline made under similar conditions are symmetrical compounds; but, as we felt it was necessary to give an absolute proof of its structure, we treated the triioddinitrobenzol with aniline, when it formed a trianilidodinitrobenzol melting at 181°. The symmetrical trianilidodinitrobenzol made by Palmer and one of us † from symmetrical tribromdinitrobenzol melted at 179°; in spite of the difference of two degrees in these melting points there can be no doubt of the identity of the compounds, and it follows, therefore, that the triiodbenzol melting at 181° has the constitution I_3 1 . 3 . 5. This would leave only the structure 1 . 2 . 3 for Istrati and Georgescu's triiodbenzol melting at 85°; but in view of the fact that this compound was isolated from a mixture of the two triiodbenzols and two tetraiodbenzols, it seems to us possible that it may be the unsymmetrical isomere (1 . 2 . 4) (melting at 77°) contaminated with some of these less fusible substances. We had hoped to prepare several derivatives of the triiodbenzol, but were unable to do so in the time at our disposal, and, as we cannot continue our work together, think it well to publish this account of the results so far obtained.

Preparation of Triiodaniline.

The triiodaniline was prepared by the method of Michael and Norton ‡ slightly modified. Ten grams of aniline were dissolved in dilute hydrochloric acid, and diluted with water at 15° or a higher temperature to the volume of seven litres. This solution was then treated with a rapid stream of air charged with the vapor of monochloride of iodine by passing it through a flask containing somewhat more than the required amount of this substance heated to about 60° by immersion in warm water. After thirty or forty minutes the action had come to an end, and the liquid was filtered as quickly as possible to remove a heavy black precipi-

* Bul. Soc. Sci. Fiz., I. 66.
† These Proceedings, XXIV. 111.
‡ Ber. d. chem. Ges., XI. 111 (1878).

tate which had formed; the filtrate was allowed to stand for several hours, when it deposited a flocculent buff-colored precipitate, the weight of which varied from 10 to 20 grams in different operations; that is, 20 to 40 per cent of the theoretical yield. An additional amount of the triiodaniline could undoubtedly have been obtained from the black precipitate, which was filtered out at first, but this was so impure that it seemed more time would be lost in purifying it than in preparing fresh quantities of the second buff-colored precipitate, which without further treatment was pure enough for the manufacture of the triiodbenzol. That it was the triiodaniline was shown by an analysis of the substance purified by crystallization from glacial acetic acid and alcohol with the aid of boneblack, which gave 81.25 per cent of iodine instead of the 80.87 per cent required by the formula. Its melting point was 185°. Michael and Norton give 185½°.

The monochloride of iodine used in this work was made by the action of chlorine on iodine according to one of the methods given by Hannay,* and used later by Bornemann.† Bunsen's ‡ method, which consists in boiling iodine with aqua regia, gave a less good result. Distillation of iodine with potassic chlorate, recommended by Schutzenberger § and Hannay,‖ was not tried. Forty-two grams of powdered iodine (the amount needed for ten grams of aniline) were treated with dry chlorine in a flask, until they had gained 12 grams; in addition to the reddish brown liquid monochloride a considerable amount of the brilliant yellow crystalline trichloride of iodine was formed, which was converted into the monochloride by adding a small excess of iodine and heating the flask gently on the steam bath under a short air condenser, until the yellow crystals had disappeared. The monochloride of iodine solidified in fine gray crystals, if cooled below 10°, and in this solid state could be kept for some time without decomposition. Its tendency to solidify made it necessary in the preparation of triiodaniline to use the solution of chloride of aniline at a temperature of at least 15° in order to avoid the danger of having the tube stopped up with monochloride of iodine. Although this substance melts at 24°.7 (Hannay), we found no trouble from solidification with a solution at 15°, which can be explained by the marked tendency of the monochloride to remain liquid after it has been melted.

* Proc. Lond. Chem. Soc., XXVI. 815 (1873).

† Ann. Chem. (Liebig), CLXXXIX. 184 (1877).

‡ Gmelin-Kraut's Handbuch, I. 2, p. 416.

§ Zeitschr. d. Chem., VI. 1.

‖ Proc. Lond. Chem. Soc., XXVI. 815 (1873).

Symmetrical Triiodbenzol, $C_6H_3I_3$.

This substance was prepared as follows: Ten grams of the buff-colored triiodaniline, made as described in the previous section, were boiled with 125 c.c. of benzol and 25 c.c. of alcohol, and disregarding the undissolved portion, 5 c.c. of commercial sulphuric acid were added, and then 5 grams of finely powdered sodic nitrite were sifted into the liquid as quickly as possible. As soon as the evolution of nitrogen had slackened sufficiently, the liquid was boiled for some time on the steam bath, until a large part of the solvents had passed off; during this boiling a bright yellow solid, which formed on the particles of sodic nitrite as they entered the liquid, changed its color to a light grayish brown. After the solution had been boiled, it was allowed to stand over night, and then the deposit was filtered out and washed, first with alcohol and afterwards with hot water, to remove the inorganic salts. The amount of this crude product rarely fell below 50 per cent of the theoretical yield.

The product, obtained as described above, was next sublimed from a large watch-glass heated on the sand bath, and covered with a funnel which stood on a piece of filter paper above the substance. If this sublimation was carried on slowly enough, as much as 80 per cent of white glistening crystals was obtained, but if it was urged too fast, the impurities also sublimed, and the crystals were yellow, or even in extreme cases light brown and sticky. When proper care was used, white crystals were obtained by this sublimation, even from very impure products, such as those recovered by evaporating the liquid portion of the product of the diazo reaction. The white sublimed crystals were not, however, pure, and to remove from them a persistent impurity we found repeated recrystallizations from alcohol were necessary, which finally raised the melting point to 181°, where it remained constant. The substance was then dried at 100°, and analyzed with the following results: —

I. 0.1187 gram of the substance gave by the method of Carius 0.1838 gram of argentic iodide.

II. 0.1453 gram gave 0.2249 gram of argentic iodide.

	Calculated for $C_6H_3I_3$.	Found. I.	II.
Iodine	83.54	83.66	83.60

Properties of 1.3.5 *Triiodbenzol.* — This substance crystallizes from alcohol at first in radiating groups composed of a few slender prisms, which develop later into long white prisms frequently tapering, but

always terminated by a single plane at an oblique angle to the sides of the prism. It melts at 181°, and sublimes easily. It is freely soluble in benzol, or carbonic disulphide even in the cold; in chloroform it is moderately soluble in the cold, freely soluble when hot; in ether it is moderately soluble, whether hot or cold; in glacial acetic acid or ethyl acetate it is somewhat soluble in the cold, freely soluble when hot; in alcohol or acetone it is slightly soluble in the cold, moderately soluble when hot; it is apparently insoluble in water, hot or cold. The best solvent for it is alcohol. Strong hydrochloric acid has no apparent action on it, even when hot; strong nitric acid also has little or no action on it, but fuming nitric acid acts on it in the way described in the next paragraph. Strong sulphuric acid, when heated with it to its melting point, causes a partial decomposition, taking on a dark color; at higher temperatures the triiodbenzol sublimes out of the mixture. A strong solution of sodic hydrate seems to have no action on it, even when boiling.

An attempt was made to prepare triiodnitrobenzol; for this purpose five grams of symmetrical triiodbenzol were boiled with 140 c.c. of a mixture consisting of four parts of fuming nitric acid with one part of common nitric acid. On cooling light yellow crystals appeared, and an additional amount of the product was obtained by pouring the acid liquid into about a litre of water, when a pale yellow flocculent precipitate was formed, which was filtered out, after it had stood some time, and with the crystals weighed 5.3 grams. This was purified by crystallization from a mixture of four parts of alcohol with one of water, until it showed the constant melting point 210°. This indicates that the substance is triioddinitrobenzol, since Istrati and Georgescu * obtained a triioddinitrobenzol melting at 210°–212° from their triiodbenzol melting at 182°–184°. For still greater certainty the substance was dried at 100°, and analyzed with the following result: —

0.2049 gram of the substance gave by the method of Carius 0.2644 gram of argentic iodide.

	Calculated for $C_6HI_3(NO_2)_2$.	Found.
Iodine	69.77	69.76

The substance, therefore, is a dinitro compound, although obtained from fuming nitric acid somewhat diluted with common nitric acid. We

* Bul. Soc. Sci. Fiz., I. 66.

did not have time to try whether the mononitro compound could be obtained with a still more dilute nitric acid.

The agreement between the melting points of our triiodbenzol, 181°, and triioddinitrobenzol, 210°, with those obtained by Istrati and Georgescu, * 182°–184° and 210°–212°, establishes the identity of these substances beyond a doubt. The triioddinitrobenzol also gives us the means of proving their constitution. For this purpose 0.5 gram of the triioddinitrobenzol were heated with 0.5 gram of aniline; this proportion gives about six molecules of aniline to each molecule of the dinitro compound. The heating was carried on for two hours on the steam bath, and the product, a dark red solution, was freed from the excess of aniline by washing with dilute hydrochloric acid, when it formed a dark red sticky mass, which was purified by working it well with a rod under dilute hydrochloric acid and then crystallizing it from alcohol. It showed the constant melting point 181°, which agrees sufficiently well with 179°, that given by Palmer and one of us † for the trianilidodinitrobenzol made from the tribromdinitrobenzol Br_3 1 . 3 . 5 . $(NO_2)_2$ 2 . 4. This proves, therefore, that the triiodbenzol melting at 181° has the iodine in the position 1 . 3 . 5, as would have been inferred from its preparation from triiodaniline, which according to the analogy of the chlorine and bromine compounds should have the symmetrical constitution.

* Bul. Soc. Sci. Fiz., I. 62, 66.

† These Proceedings, XXIV. 111.

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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY
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A STUDY OF GROWING CRYSTALS BY INSTANTANEOUS PHOTOMICROGRAPHY.

By Theodore William Richards and Ebenezer Henry Archibald.

With Three Plates.

Investigations on Light and Heat, made and published wholly or in part with Appropriations from the Rumford Fund.

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A STUDY OF GROWING CRYSTALS BY INSTANTANEOUS PHOTOMICROGRAPHY.

By Theodore William Richards and Ebenezer Henry Archibald.

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Countless observers have watched the growth of crystals under the microscope. As long ago as 1839 attempts were made to study also the birth of crystals, in order to determine in what manner the new phase makes its entrance into the system. With a microscope magnifying 600 diameters, Link * thought he could detect the formation of minute globules at the moment of precipitation, — globules which soon joined and assumed crystalline form. Schmidt, † Frankenheim, ‡ and especially Vogelsang, § made similar observations some years later, and several more recent accounts of this phenomenon have appeared. Modern investigators have been more concerned with the *speed* of separation from supersaturated or supercooled liquids than with the *form* of the first separation.‖

Ostwald, in 1891, accepted the interpretation of these data, which assumes that crystallization is always preceded by the separation of an initially liquid phase, consisting of a supersaturated solution of the former solvent in its former solute.**

This explanation is indeed a plausible one, and undoubtedly holds true in cases like those studied by Schmidt and Vogelsang, where a substance separates at a temperature not far below its melting point, and often where a substance soluble in one liquid is precipitated by the

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* Link, Pogg. Ann., **46**, 258 (1839).

† Schmidt, Lieb. Ann., **53**, 171 (1845).

‡ Frankenheim, Pogg. Ann., **111**, 1 (1860).

§ Vogelsang, Die Krystalliten (Bonn, 1875). See Lehmann, Molecularphysik, I. p. 730 (1888).

‖ Gernez, Compt. Rend., **95**, 1278 (1882); Moore, Zeits. phys. Chem., **12**, 545 (1893); Friedländer and Tammann, ibid., **24**, 152 (1897); Tammann, ibid., **25**, 441; **26**, 307, 367, **28**, 96; Küster, ibid., **25**, 480, **27**, 222; Bogajavlensky, ibid., **27**, 585.

** Lehrbuch, I. 1039 (1891).

addition of a consolute liquid in which the substance is insoluble. For examples, phenol always separates from aqueous solution in the form of a liquid, and manganous sulphate forms at first two liquid phases when alcohol is added to its aqueous solution. On the other hand, the separation of a high-melting salt like baric chloride from its solution in pure water is much less likely to take place in this way. The admixture of water necessary to lower a melting point from 900° to 25° would be so large as to make the new phase, a solution of water in baric chloride, supersaturated to an improbable extent. It is hard to guess where the line between probability and improbability should be drawn.

Ostwald has shown that an exceedingly small particle of solid is capable of starting crystallization, * — a fact which may not be wholly foreign to the present discussion.

In any case, the matter seemed worthy of further experimenting. Ostwald says, "Die erste Bildung der Krystalle lässt sich bei Salzlösungen und dergleichen microscopisch nicht verfolgen, weil gewöhnlich im Gesichtsfelde an einer bislang gleichförmigen Stelle plötzlich ein Krystallchen erscheint." While this is true as far as the human eye is concerned, instantaneous photography, an art unknown in Link's time, seemed peculiarly fitted for the unprejudiced recording of the circumstances attending the genesis of crystals. An attempt in this direction is described below.

The problem resolved itself into the taking of a number of successive instantaneous microphotographs of a suitable mixture at the point of crystallization. This problem presented some difficulties, however. In order to secure a sufficiently brief exposure, very great illumination is needed. The greater the magnifying power of the lenses of the microscope-camera, the more intense must be the source of light. The difficulty is increased by the fact that most crystals are so transparent as to absorb but little light, and reflection is possible only in certain directions. Hence it is hard to obtain a distinct image even in a strong light. Moreover, the machinery necessary for shifting the plates must be so frictionless in construction, and so firmly fixed, as to impart no vibration to the camera or the mobile subject of study.

These difficulties were at least partially overcome by two different arrangements, the first of which caused the successive impression of a bright image in a dark field, and the second registered dark images in a succession of bright fields. Obviously the former was the more economical as

* Ostwald, Zeits. phys. Chem., **22**, 289 (1897).

regards expenditure of sensitized film, and the more simple in execution; for when the field is dark, successive images can be obtained by a very slight motion of either object or film, while, when the field is light, the whole previously exposed surface must be replaced by a fresh surface before each exposure.

The apparatus consisted of a good compound microscope fitted above with a vertical folding camera, which was supported by two massive steel pillars on the heavy stand. It was, in short, the regular photomicrographic outfit made by Bausch and Lomb. Between the microscope and camera, in a suitable light-tight box, was placed a revolving shutter, which allowed an exposure equal to one fifth of the time of its revolution. Thus, when the shutter made two revolutions in a second, the exposure was one tenth of a second. A Henrici hot air motor, combined with speed-reducing double pulleys, enabled the experimenter to use any rate of revolution desired. The rate was reasonably constant, but no attempt was made to make it absolutely so. The sensitive plate or gelatine film was held above in a suitable holder, which was put in the place of the ground-glass plate used for focusing just before each series of exposures.

In carrying out the first of the two methods it was found more convenient to move the crystallizing solution than to move the photographic plate. For this purpose the slide bearing the drop of liquid was attached by a wire to a point just below the centre of a segment provided above with saw-teeth. The segment was moved gradually by the oscillating motion of a connecting-rod, fastened by a crank to the revolving shutter at one end and playing into the saw-teeth on the other. In order to make the motion certain, the stroke of the connecting-rod slightly exceeded the distance between the saw-teeth. The segment was suspended in such a way that its centre of gravity coincided with its point of support, and the friction of its bearings was so adjusted that it would move easily, and yet remain stationary during the return stroke. The distance through which the observed object was moved was easily varied by altering the relative lengths of the lever-arms; distances varying from one tenth to one fiftieth of a millimeter were usually used. The shutter was so arranged that during the exposure the segment and slide were at rest, the shift in position being effected during the four fifths of the revolution through which the shutter was closed. The accompanying diagram will make the arrangement clearer.

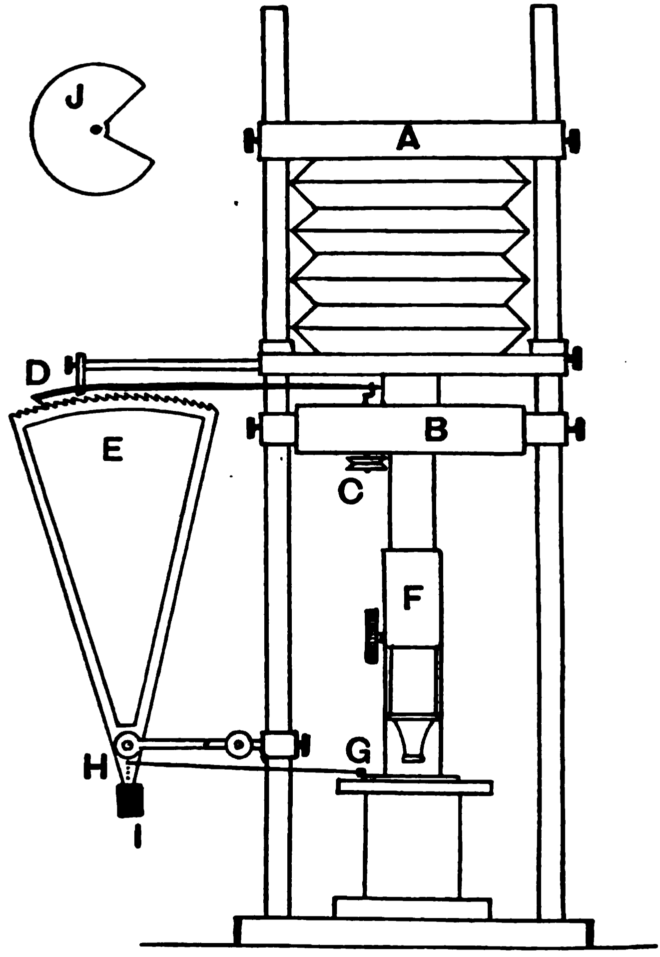

Figure 1. Diagram of Photographic Apparatus. (½ natural size.)

A, sensitive plate or film holder.
B, box containing shutter.
C, pulley attached to axle of shutter to communicate power from motor.
D, light rod moved by crank attached to same axle; D is guided by a stout support in which it moves loosely.
E, segment provided with ratchet-teeth; moved gradually by rod D.
F, microscope.
G, slide for object, moved by wire running to H.
H, holes to regulate amplitude of object's motion.
I, weight, balancing segment.
J, horizontal projection of revolving shutter in detail.
The diagram represents the apparatus an instant before an exposure begins.

As a source of light any ordinary combination of incandescent electric lights proved to be inadequate. A good Auer von Welsbach light with a powerful reflector was more satisfactory, but the best results were obtained with the help of sunlight directed by a suitably arranged mirror and condensed by reflectors and lenses. The chief, though not serious, difficulty of this arrangement was the great heat caused by the converging rays, a difficulty which was obviated partially by an absorbent screen in some later experiments.*

The first photographs were taken by reflected light, the drop of solution being placed upon a ruby-colored slide. As soon as the crystallization had begun upon one edge of this drop, the very sensitive plate was uncovered and the shutter and segment were set in motion. The exposure was stopped after fifteen or twenty revolutions, so as to avoid confusing superpositions. Even with the strongest light the images were very faint and unsatisfactory; it is not worth the space to reproduce them here.

Another mode of obtaining light images on a dark ground, applicable to all except the isometric system of crystals, is the use of polarized light.† A Nicol prism was placed in the barrel of the microscope, and another just below the stage. The main body of the light was thus intercepted by the crossed prisms, and only that which had been deflected by the crystalline structure was allowed to emerge. It is true that this method could not in all probability decide the chief point at issue; for the prenatal globular condition of crystals would probably have no effect on polarized light. Definite optical structure is of course necessary to produce the required deflection of the plane of polarization, and such definite structure might not be possessed by the globules. Nevertheless, the idea seemed well worth a trial.

The images were now much more clearly defined and striking, and with a magnification of 30 diameters, ten sharp impressions, each exposed $\frac{1}{50}$ second, could be obtained in a second. For this low power the eyepiece was removed from the microscope and an objective with long focal distance alone was used to give the image. The degree of enlargement was obtained by actually measuring the image of a micrometer scale divided into $\frac{1}{10}$ millimeters. The rapidity of exposure was so great that many plates were sacrificed, for it was difficult to find the precise moment when nascent crystals were in the field of view. In most cases the crystalliza-

* Hutchins has shown that pure water is as good as a solution of alum for this purpose (Am. J. Sci., **143**, 526 [1892]).

† This suggestion was kindly made by Professor E. C. Pickering.

tion was already well started when the exposure began, as in Figure 4; but in some nothing but blank negatives were obtained. The best method is so to arrange circumstances as to have the crystallization begin upon one edge and spread slowly over the drop. Another difficulty was the attaining of the exact actinic focus, which differed slightly from the visual focus. It was found that a definite fraction of a revolution in the fine adjustment of the instrument could be relied upon to cover this difference, when experiment had once found the right spot.

Among other substances sodic nitrate, baric chloride, cupric sulphate, and ferrous ammonic sulphate were found to give satisfactory results. A few photographs chosen as being typical examples of many negatives are given here. (Plate I. Figs. 2, 3, 4, 5.)

All the images recorded on these plates are perfectly sharp and regular when in focus; but the magnifying power was too low to give important evidence concerning the birth of the crystals. The crystals always first appear as points, indicating a diameter of less than $\frac{1}{300}$ millimeter. The regularity of growth of those already well started is worth a passing mention.

The next objective used gave a magnification of 110 diameters. With this power the light was so much diminished that exposures of less than $\frac{1}{15}$ second became too pale. Three examples from among these negatives are given below. It will be noticed that in all cases the crystals have their regular forms when they first appear upon the plate. Another point worthy of attention is the fact that the growth in diameter at first is more rapid than it seems to be subsequently. This rapid growth of small particles has already been noticed by Ostwald;* it is treated more fully in the following pages. The crystals of sodic nitrate grew faster than those of baric chloride or cupric sulphate, and the two latter substances evidently appeared at first in very thin plates. It is interesting to note that the thickening of these plates caused a corresponding change in the quality of the emerging light, and hence the crystal-images show a rhythm of dark and light. (Plate I. Figs. 6 and 7, Plate II. Fig. 9.)

At this point the whole method of procedure was changed on account of the probability that a globular condition, if it existed at all, would not be visible through the crossed Nicols. The apparatus was now arranged for the exposure of successive portions of a film to unpolarized sunlight emanating from a bright field, upon which the crystals appeared as dark spots. The slide and crystallizing solution were allowed to remain sta-

* Ostwald, Zeits. phys. Chem., **22**, 320.

tionary, and the gelatine film was moved, as it is in the common film-cameras. The $2\frac{1}{2}$ inch Eastman cartridge film was found to answer the purpose. At first the turning was effected by an automatic electro-magnetic arrangement which received its current from a make-and-break contact attached to the shutter. Since a current of ten amperes was needed to secure a sufficiently forcible and speedy action, the operation of this device was somewhat troublesome, and when the exposures were not much more frequent than one a second the film was rolled by hand. A suitable signal attached to the shutter axle, which was still turned by the Henrici motor, gave the necessary indication of the proper moment for renewing the sensitive surface. With this apparatus it was of course possible to obtain photographs of isometric crystals, which could not be examined with the preceding arrangement.

At first a power of 100 diameters was employed, and very satisfactory pictures of the growth of crystals of potassic iodide were obtained. One of these negatives is reproduced here as an example. (Plate II. Fig. 9.) They showed nothing new, however; hence a much higher power of 580 diameters was applied by combining a "2 inch" eyepiece with an "$\frac{1}{8}$ inch" objective. With this contrivance the light was of course far less intense, and the definition less sharp. Even with the brightest sunlight, concentrated by mirrors and an Abbe condenser, the exposure could not profitably be made less than $\frac{1}{8}$ second. These plates have been enlarged by usual processes to over seven times their original size, so that a total enlargement of over four thousand diameters has been attained. Since these larger images are not much more clear than the smaller ones, while they occupy much more space, the plates herewith given are all from the original negatives.

A number of good impressions of crystallizing potassic iodide were taken under these circumstances, but many other rolls were sacrificed. The chief difficulty, as before, was to secure the right moment; and this difficulty was of course much augmented by the limited expanse of the field. Prints from a few of the successful negatives are given below. In order to give a clear impression in printer's ink, these were much intensified by successive photographic printing and intensification; but of course no attempt was made to remove the imperfections of the successive plates, for which allowance may easily be made. (Plate III. Figs. 10–15.)

The study of these photographs reveals several interesting points. In the first place, it is noticeable that no image is wholly without evidence of crystalline structure. The most doubtful cases are those in Figures 9 and 11; but the elongated shape of these doubtful images seems to

indicate a solid. A globule of a new liquid phase, $\frac{1}{1000}$ millimeter in diameter, would have left an unmistakably circular image on the highly magnified plate, for its index of refraction could not have been identical with that of the aqueous solution. The fact that we could not find such a globule of course does not prove that a globule cannot exist, either for an infinitesimally brief period of time, or of an infinitesimal magnitude beyond the reach of microscopic observation. Nevertheless, so many scores of photographs were taken as to diminish considerably the probability that such globules can ever be seen with substances possessing a high melting point.

A striking fact to be noticed in nearly all the most highly magnified records is the ill-defined appearance of the smallest crystals. This appears to be due, not to a lack of structure, but rather to the rapid growth in diameter which is manifest in the young crystal. The initial rapidity is so great that the fifth of a second appears to include several different stages of growth, and hence a blurred impression results. It is easy to obtain some idea of the rapidity of this initial growth by comparing the sizes of the first two or three appearances of each crystal.

With this object a few of the series were measured by means of an accurate micrometer; but the conditions of the experiments are too uncertain to give the very precise measurements much value. Perfect constancy of temperature and evaporation, as well as in the rate of the revolving shutter, involving grave complications in the apparatus, should of course be maintained if great accuracy is attempted. Measurements with a fine millimeter scale afford all the precision which it is worth while to attain under present conditions. A typical case (Figure 9, largest crystal) gave the following measurements in millimeters for the successive longest diameters: 2.0; 2.6; 3.0; 3.2; 3.3; 3.5; 3.7; 3.9; 4.1; 4.2; 4.4. The actual sizes of the crystals were of course only a hundredth of these measurements, since the enlargement was 100 diameters.

In spite of the inexact nature of such measurements, it is possible to use them as a means of defining approximately the law regulating the changes in speed. The following table details six series of corresponding diametric measurements of six crystals taken at random. The measurements were taken directly from the photographs, in millimeters.

Diameters of Successive Images.

	Crystal 1.	Crystal 2.	Crystal 3.	Crystal 4.	Crystal 5.	Crystal 6.
First appearance.	1.0	2.0	3.0	3.0	4.0	2.5
Second appearance.	1.6	2.6	5.7	6.0	6.7	3.5
Third appearance.	1.7	3.0	6.8	7.0	7.3	4.1

These all show greater growth in the first interval than in the second. In order to reduce them to one standard, the diameter of the third appearance was taken in each case as unity. The table then becomes: —

Diameters of Successive Images.

	Crystal 1.	Crystal 2.	Crystal 3.	Crystal 4.	Crystal 5.	Crystal 6.	Average.
First appearance.	0.59	0.67	0.44	0.43	0.51	0.61	0.54
Second appearance.	0.94	0.87	0.84	0.86	0.86	0.85	0.87
Third appearance.	1.00	1.00	1.00	1.00	1.00	1.00	1.00

At the time of the first appearance, the average age of the crystal must be about half the time intervening between two exposures; for the crystal must have been formed since the last exposure, and it is as likely to come near the beginning as near the end of the interval. Thus in Figure 11 the crystals evidently started immediately after the previous exposure, while in Figure 9 they were registered while still very young. The averaging of a much larger number of observed diameters led to the slightly different values given below, corresponding to the accompanying times: —

Time = t.	Diameter = D.
0 interval	Diameter 0
0.50 interval	Diameter 0.57
1.50 intervals	Diameter 0.87
2.50 intervals	Diameter 1.00

These data are plotted in Figure 16.

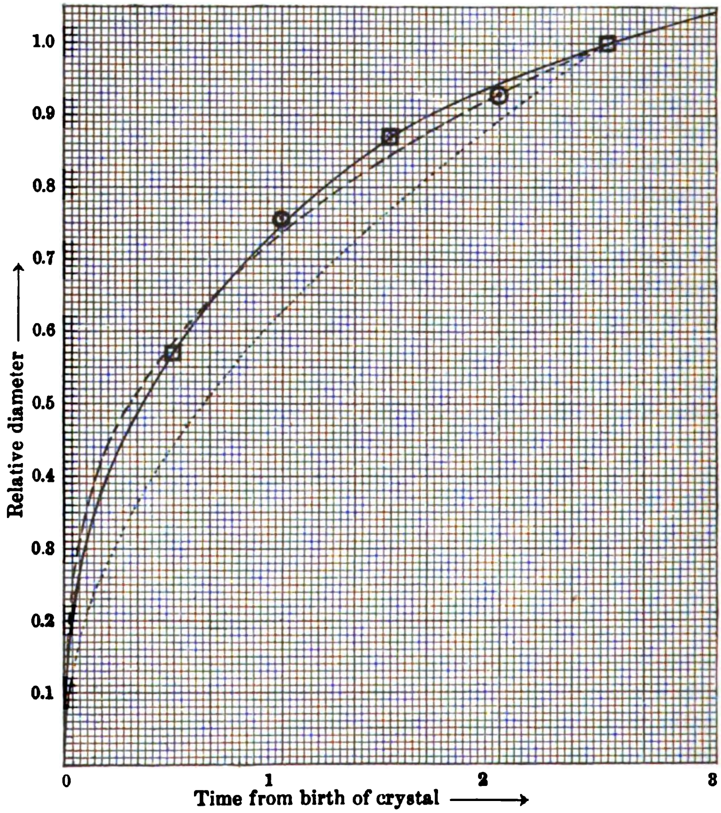

FIGURE 16. DIAGRAM REPRESENTING RATE OF INCREASE IN CRYSTAL DIAMETER.

□ represents point from average of crystals taken at random.
○ represents point from average of selected crystals.
——— represents probable actual rate of growth.
— — — represents equation $D^3 = kt$.
.... represents equation $D^2 = kt$.
The unit of time is the time of one revolution of the shutter, or 1.25 seconds.
The substance was potassic iodide.

The inspection of the figure shows at once that the curve is similar in general shape to one represented by the equation $D^n = kt$, where D is

the diameter of the crystal, t the time from the birth of the crystal, and k a constant. The only question is as to the magnitude of n. The curves which result from the assumptions $n = 2$ and $n = 3$ are given above, for comparison with the experimental curve. It is clear that the curve with the latter value, $n = 3$, is the nearest, possessing the same general curvature, and deviating from the average less than the individual measurements do. This is equivalent to saying that *equal increments of time correspond to equal increments of volume*, instead of equal increments of *surface*, as one might have supposed. Of course a law based upon such merely approximate data cannot be considered as definitely settled; but clearly the general character or tendency of the curve is established. It is probable that under the necessarily ill-defined conditions of our experiments the growth follows no one law with precision; supersaturation, convection, diffusion, and evaporation must all influence the result. The crystal which seems to have deviated most widely from the average is that depicted in Figure 10; this crystal grew at first less rapidly than usual, and finally came almost to a standstill. It is possible that an increasing solubility due to increasing temperature may have caused this delaying tendency

It is interesting to compare this average, calculated on the assumption that the crystal starts in the middle of the dark interval, with a few single cases which appear to have begun to crystallize very near the beginning or end of the interval. In these cases, the first image of the crystal will appear either almost as large as the second image, or very small compared with it. It will appear almost as large as the second image when the preceding exposure has just not caught the beginning of the crystal, which has thus had a whole interval for growth; or very much smaller than the second image when the first impression has registered a crystal only a very small fraction of a second old. Marked examples of the former case are to be found in Figure 11, and of the latter in the largest crystal in Figure 9, and the smallest crystal in Figure 15. The times of revolution represented by Figures 9 and 11 are the same, 1.25 seconds, and the other conditions also were identical, hence we may compare these with accuracy. Careful measurements of the sizes in Figure 9 showed the first large impression of the crystals to be about eighty per cent of the diameter of the next impression, and approximately the same relationship appears in Figure 11. In order to find if this relationship corresponds with the equation $D^3 = kt$, the larger diameter is assumed to be 0.93, the theoretical value corresponding to two intervals of time, if that corresponding to two and one half intervals is taken as unity. Hence the smaller one

becomes 0.75, corresponding to one interval of time, a value, marked in a circle on the diagram, which is surprisingly near the cubic curve. Hence the equation $D^3 = kt$ is confirmed. That the same curve holds approximately for the further growth of the crystal is manifest by a quantitative study of Figure 9 (Plate II.).

In this connection it is interesting to note that the crystal seems often to grow at first in the same *proportion* in all directions. Even the very minute image in the centre of the second exposure, given in Figure 9, shows itself under the microscope to be elongated like the crystal which grows from it. In the next exposure this crystal had the proportions 0.02 mm. × 0.0125 mm., and after four more exposures it still had almost exactly the same proportions, being 0.035 mm. × 0.022 mm. After two or three more seconds the form given in Figure 9 began to change slightly, the crystal becoming slightly less elongated in shape; but by this time the neighboring crystals had grown so much as to approach it, and hence to alter the conditions. A similar constancy in proportion may be observed in many other series here given.

The diagram shows how exceedingly fast the diametric growth of the crystal must be in the first tenth of a second of its existence. Hence we have an explanation for the suddenness of its appearance to the eye of an observer, and for the blurred edges of its photographic image. It is true that another cause may contribute to the blurred effect; namely, the irregular refraction caused by the convection of the lighter solution which has just deposited part of its load; but the speedy growth alone is capable of explaining the observed indistinctness.

Interesting as the rapid initial growth in diameter may be, it places a serious bar in the way of more precise study of the birth of crystals. One clearly needs not only high magnifying power, but also great speed; and these two together require very intense light. Whether or not we shall be able to obtain more positive knowledge with the present apparatus, is a questionable matter. The same phenomenon casts a measure of doubt over some of the observations of Link and his followers. Is it not possible that the subjective effect of the rapidly growing crystal might be mistaken for that of a globule of liquid? Even upon the photographic plate there is a slight resemblance, and in one or two cases deliberate study is needed to detect evidence of structure in the smallest crystals.

In conclusion, the report of the foregoing pages may be summarized as follows. It has been found possible to take very frequent photomicrographs of crystals during their birth and growth. An enlargement of over four thousand diameters was obtained, and both common and polar-

ized light were used. Only substances with high melting points were examined, and the crystallization was always from aqueous solution. No properly focused image on any of the plates seemed to be devoid of crystalline structure. The growth in diameter during the first second of the crystal's life was found to be vastly greater than during the subsequent period. Not the diameter itself, but a power of the diameter, was proportional to the time under the conditions used in our experiments. This exceedingly rapid initial diametric growth accounts for a lack of definition noticed in the first images, — a lack of definition sufficient to have misled the eye, but not enough wholly to obscure the photographic evidence of crystalline structure.

Hence we may conclude that whatever theoretical reason there may be for believing that crystals always develop from a transitory liquid phase, the present experimental evidence is inadequate to prove that these globules attain a size visible in the microscope, except in the case of substances which melt at temperatures not far from the temperature of crystallization. The present paper is to be regarded rather as the suggestion of a mode of study than as a finished treatment of the subject, however.

The apparatus might be used to obtain a series of kinetoscopic pictures of insects or other small animals or plants, and is now being used for the study of the change in structure of steel at high temperatures.

CAMBRIDGE, MASS., *October*, 1898, to *October*, 1900.

FIGURE 2. Baric chloride; 30 diam.; exposure 0.04 sec.

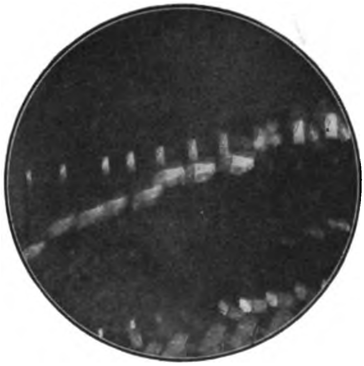

FIGURE 3. Baric chloride; 30 diam.; exposure 0.08 sec.

FIGURE 4. Sodic nitrate; 30 diam.; exposure 0.10 sec.

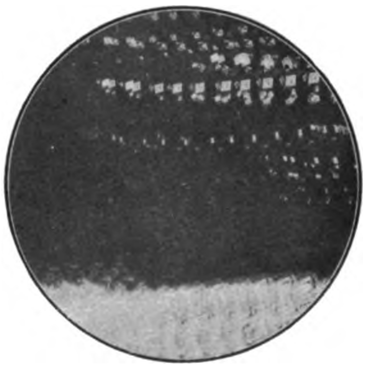

FIGURE 5. Sodic nitrate; 30 diam.; exposure 0.12 sec.

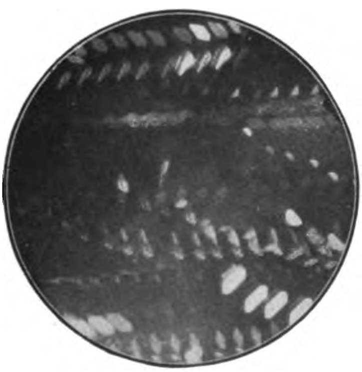

FIGURE 6. Baric chloride; 110 diam.; exposure 0.10 sec.

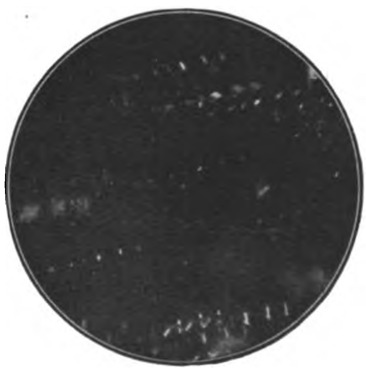

FIGURE 7. Cupric sulphate; 110 diam.; exposure 0.12 sec.

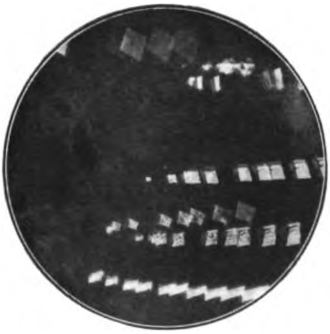

FIGURE 8. Sodic nitrate; 110 diam.; exposure 0.12 sec.

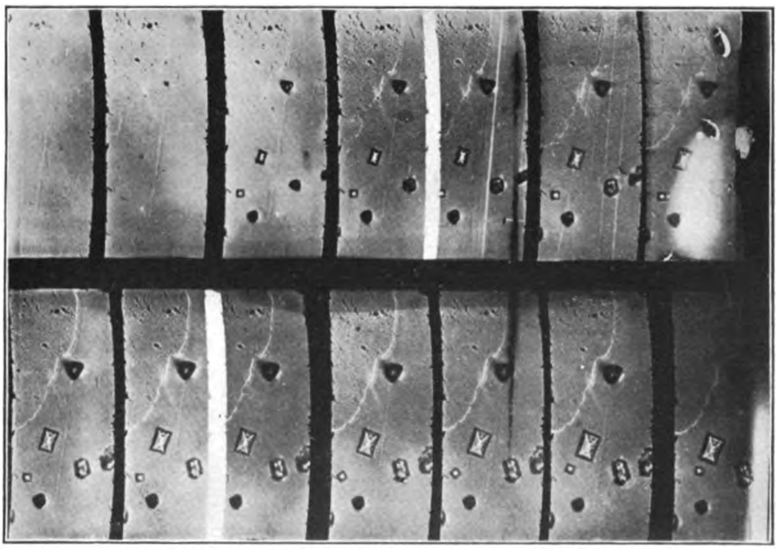

FIGURE 9. Potassic iodide; 100 diam.; exposure 0.25 sec.

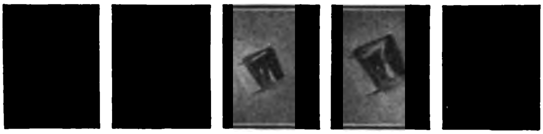

FIGURE 10. Potassic iodide; 580 diam.; exposure 0.17 sec.

FIGURE 11. Potassic iodide; 580 diam.; exposure 0.25 sec.

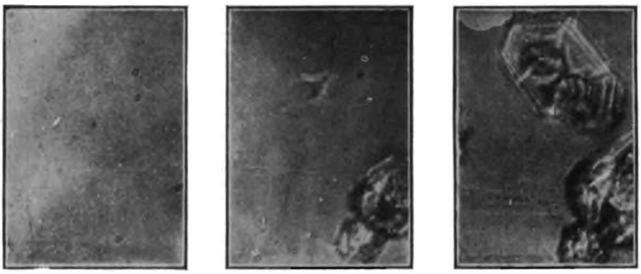

FIGURE 12. Potassic iodide; 580 diam.; exposure 0.17 sec.

FIGURE 13. Potassic iodide; 580 diam.; exposure 0.17 sec.

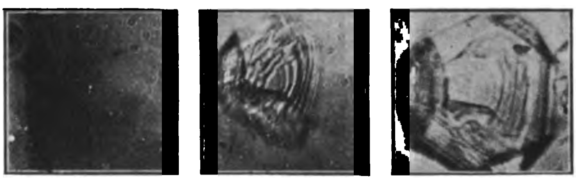

FIGURE 14. Potassic iodide; 580 diam.; exposure 0.17 sec.

FIGURE 15. Potassic iodide; 580 diam.; exposure 0.17 sec.

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DESIGN AS A SCIENCE.

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DESIGN AS A SCIENCE.

By Denman W. Ross, Ph. D.

Presented January 9, 1901. Received January 12, 1901.

Art may be defined as the expression of Life, or, more specifically, as excellence in the matter of expression; and excellence, in this case, may be defined as consistency, a consistency in forms of expression. Consistency has many manifestations, but they fall under three principal heads: Balance, which is a consistency of oppositions (antitheses); Rhythm, which is a consistency of association (joint action or movement); and Harmony, which is a consistency of character (likeness). If art is consistency in forms of expression, Balance, Rhythm, and Harmony are its principles. They are also the principles of Beauty. We have no other definite conception of beauty. It is a perfect relationship or connection of parts in one organic whole. We find this unity in nature, when we seek it, and we find it in the art of man, *homo additus naturæ.* Wherever and whenever we find it, we have the perception of beauty.

The idea which the Greek philosophers had of art was as nearly as possible the one which I have given as the major premise of this argument, and it is in the art of the Greeks that I have found its most perfect illustration. See Plato, in the Gorgias (§ 504): "The artist brings all things into order, making one part to harmonize and accord with another, until he has constructed a regular and systematic whole; this," Socrates says, "is true of all artists." Aristotle expresses the same idea when, in his Poetics, he speaks of poetic imitation having "as its subject, a single action, whole and complete, with a beginning, a middle, and an end. It will thus," he says, "resemble a living organism and produce its proper pleasure." See Poetics, xxiii. 1.

While consistency in forms of expression may be regarded as a definition of art, it is not, of course, a definition of what is significant or important in art. We can take a few lines and put them together so that they shall be absolutely consistent, expressing one idea, unmistakably. The result is a work of art, but the work is unimportant. It is an easy thing to do. The work of art is important in proportion to the number

and variety of elements which are reconciled and united in its idea. Consider, for example, Raphael's Dispute of the Sacrament. Think of the number and variety of the elements united in that great composition. Such a design is an achievement representing intellectual power of the very highest order. So we discover, as the principal factor in art, the mind of the artist, and the measure of this is observed in his ability to see in many things one idea, and to express in one idea many things. Beyond this power of the mind to grasp and express many things in single ideas, a power which we can analyze, understand, and appreciate, lies something which defies analysis, something which we may appreciate, but which we cannot understand. This is the strictly personal element which goes into the work of a man, which stamps it as his, which distinguishes it from the work of other men. This personal element, when it is important, we call genius. The genius of the artist in his art is constantly mistaken for the art itself. It seems to me that the genius of the artist is something which lies beyond his art. His art is simply the technique in which, and through which, his genius finds expression. In speaking of art, therefore, I am speaking of the technique of expression and nothing more than that. That is a matter of precise definition and analysis. There is a passage of Plato in the Philebus (§ 55), where Socrates says, "If arithmetic, mensuration, and weighing be taken from any art, that which remains will not be much." In talking about art and its principles, I mean art in this definite sense. There is a passage in the eleventh canto of the Inferno of Dante which is significant in this connection: "If you read your physics attentively [Dante refers here to the physics of Aristotle], you will discover, after not many pages, how your art follows that [physical science] just as far as it can, as the disciple follows the master."

There are many arts, the different modes and forms of expression: gymnastics (including dancing); music, speech (including poetry); construction (including architecture); modelling (including sculpture); and painting (including design). The particular art to which your attention is called in this paper is the art of painting, in its highest form, Design. Painting may be defined as expression by spots of paint, paint being in this case any coloring material, no matter what it is, that may be used. Design is painting with particular reference to the principles of art. We have painting as Design and painting as Representation, which is the definition of visual impressions, a description of things seen, remembered, or known, and we have Design in Representation. Design in which there is no representation, or in which the elements of representation are not

considered as such, may be called Pure Design. This may be defined as the arrangement or composition of spots of paint for the sake of balance, rhythm, and harmony; for the sake of consistency, unity, beauty. Pure Design appeals to the eye just as music appeals to the ear. The term of expression in music is the sound; the term of expression in design is the spot of paint.

The spot of paint is three things: it is a tone, a measure, and a shape. By *tone* I mean the pigment material used in drawing the measure of the spot and its shape. By *measure* I mean the area covered by the spot, its size. By *shape* I mean its outline, or contour. Put a spot of paint upon a piece of paper, then change (1) its tone alone; (2) its measure alone; (3) its shape alone; (4) its tone and measure, leaving its shape unchanged; (5) its measure and shape, leaving its tone unchanged; (6) its tone and shape, leaving its measure unchanged; (7) change its tone, its measure, and its shape, producing an altogether different spot.

Taking the spot of paint as the subject of my investigation, I will consider, first, the element of tone, then the element of measure, and, lastly, the element of shape. In order to study the element of tone we must eliminate all differences of measure and of shape, which might be confusing. Producing as many different tones as we can, in circles of half an inch diameter, we find that we can produce a very great number and a very great variety. Looking over the tones we have produced, we observe that every tone is relatively light or dark. It has what is called value. It is a measure of light in the white-to-black scale. Observe, also, that every tone has a color. It is red, or green, or violet, or some other color, and the color which it has is relatively intense or neutral, or it may be quite neutral. We shall find it convenient to regard the neutral as a color. It is the color of white, or gray, or black. Tone means, according to these observations, two things, — value and color.

We will consider, first, the element of value, afterwards, the element of color. In considering values alone we must eliminate all differences of color which might be confusing. Take the neutral pigments, white and black, and see how many neutral values you can produce in circles of half an inch radius. You can produce seventeen certainly, and perhaps a few more. You will observe that in producing as many as seventeen neutral values you are nearing the limit of visual discrimination, the limit of distinct definition, or expression. Observe that every value which you have produced is a force drawing attention to itself. Observe that different values exert different degrees of attractive force, that this force is determined in each case (other things, measure, shape, and color, being equal)

by its contrast with the ground-tone upon which it has been drawn. If the ground-tone is white paper, the value having the greatest attractive force is black; if the ground-tone is a half-tone between white and black, the forces of white and of black are equal. What is the result of all these forces of attraction, as they act upon the eye? The eye is held at rest at their centre of equilibrium. Where is that centre? In order to answer this question, we must bring the values into a scale-relationship upon a common ground-tone, otherwise we have no means of measuring their respective contrasts, or the forces of attraction which depend upon their contrasts. Make a scale of seventeen values, exclusive of white and black, in seventeen circles of half an inch radius, in a straight line, half an inch apart, and upon a ground-tone of the middle value. Be sure that the values are at equal intervals of equal contrasts. In order to get them into the perfect scale-relation which this implies, establish the extremes first, then the mean between the extremes, then intermediates, until the scale is complete. The interval or contrast between value and value may be great or small; the scale may be central in pitch, high in pitch, or low. It is central in pitch when its middle value is at the half-point between white and black. Considering the scale of values which you have produced, you observe what you have observed before, that each value is a force of attraction, that this force, other things being equal, depends upon the contrast with the ground-tone. The only value which has no force of attraction is the central one of the scale, the value which coincides with the ground-tone and cannot be distinguished from it. Looking at the scale again, pick out the values which have the same force of attraction. They will be those at equal distances from the half-tone, which is the ground-tone, making equal contrasts with it. In order to distinguish the different values of the scale, we will call the middle value zero (0). The values above the middle value we will call 1, 2, 3, etc., *above*. The values below the middle we will call 1, 2, 3, etc., *below*. The values above can be written thus: $\underline{1}$, $\underline{2}$, $\underline{3}$, etc.; the values below thus: $\overline{1}$, $\overline{2}$, $\overline{3}$, etc. The values having the same force of attraction are, then, those having the same numbers: $\frac{1}{1}$, $\frac{2}{2}$, $\frac{3}{3}$, etc. The numbers are the measures of the contrasts, and of the forces of attraction depending upon the contrasts. If now we scatter our seventeen values over the ground-tone of the middle value we shall be able to discover the centre of equilibrium of their forces, that is to say, the point where the eye is held by them. We have simply to remember the familiar principle of balance; that equal attractions balance at equal distances on a line connecting their centres;

while unequal attractions balance in the same way, but at distances which are inversely proportional to them, as attractions. Measures, shapes, and colors being equal, values alone differing, values $\underline{4}$ and $\underline{1}$ balance on value 0, at distances 1 and 4 respectively. If the ground-tone were $\underline{2}$ instead of 0, $\underline{4}$ and $\underline{1}$ would balance on 2, at distances 1 and 2 respectively. In this explanation of the balance of values we find the principle upon which the designer proceeds when he wishes to create such a balance. He may prefer to depend upon his visual feeling, but his feeling must be guided by the law of balance whether he thinks of the law or not.

The scale of values is not merely a scale of visual attractions to be balanced, it is also a rhythmic movement of values. The scale-relationship is not, properly speaking, a relationship of opposition or antithesis; it is one of association or joint action. The values of the scale combine to lead the eye in a movement from light to dark, or from dark to light, and this movement is easy in proportion to the perfection of the scale. If the scale is imperfect, if the intervals are not equal intervals of equal contrasts, we have the same discomfort that we have in walking on the irregularly placed sleepers of a railway track. We all know how tiresome it is to do that. Not only is the eye led in the scale of values from dark to light and from light to dark, but if the values be squeezed together the eye is led quickly or abruptly; if they are pulled apart the movement is comparatively slow or gradual. By changing the direction or the shape of the scale of values the eye may be led in different directions, and its movement may take a variety of shapes. A few simple diagrams would show the rhythmic character of the scale of values in these several aspects. Values are in harmony when they are in the same scale, and when the relations of the scale can be felt, visually. The least contrast of the scale is a factor of the greatest, and when this relation is distinctly felt we have a perception of harmony. The most perfect harmony is that of corresponding values.

Tone, as we have seen, means two things: value and color. We have been considering the element of value. We will now consider the other element, color. In order to do that satisfactorily we must eliminate all differences of value. Producing as many differences of color as we can, all in the same value (the half-tone between white and black), and all in the same measure and shape (the circle of half an inch radius), we shall find that we can produce perhaps twelve differences of color, and in each color a certain number, perhaps eight differences of intensity. In order to study color without being confused with the differences of intensity, let us put all the colors not only in the same value, but in the same degree

of intensity, the greatest intensity possible to the pigments on our palette. This being done, we shall observe, at once, that the colors have a natural order or connection with one another. Red passes into green through yellow; yellow passes into blue through green; and blue passes into red through violet. There is, in other words, a natural relationship for all the colors we can produce in the same value and intensity. There is a natural scale of colors, as there was a natural scale of values. This scale of colors is, of course, the scale of the spectrum. The spectrum which I have followed in this investigation, is the normal spectrum, the spectrum of the grating, not the spectrum of the prism. The difference is explained by Rood, by Lommel, and by other writers. Reading the spectrum from the red end towards the violet end, the colors follow one another, approximately at equal intervals of equal contrasts, as follows: red, suggesting Chinese vermilion; yellow, suggesting aureolin; green, suggesting emerald green; blue, suggesting cobalt with a little emerald green in it; violet, suggesting ultramarine with a little rose madder in it. Beyond the violet end of the spectrum we may observe the color which we call purple. It suggests rose madder with a little ultramarine in it. This color does not belong in the spectrum series. It is due to the overlapping of the red and violet ends of the spectrum. It is, however, a color which we must use, and if the primary or important colors of the spectrum are red, green, and violet, purple exists for us as an intermediate between red and violet, just as yellow is intermediate between red and green, and blue between green and violet. Between the six colors, red, yellow, green, blue, violet, and purple, come intermediates and the intermediates of intermediates up to the limit of visual discrimination. Setting the normal spectrum upon the circumference of a circle, with purple as a connecting link between the ends, the interval between any two colors can be described as an interval of so many degrees. We have an interval of 60°, the interval separating red from yellow, yellow from green, green from blue, blue from violet, violet from purple, adjacents in the scale of six colors. We have the interval of 120° between the adjacents of a scale of three colors, — red, green, and violet, for example; and we have the interval of 180° between the adjacents in the scale of two colors, — red and blue, for example. This is the greatest possible interval. It is the interval between colors opposite one another in the circle, the colors which we call complementaries. In order to study the various intervals of the scale of colors with certain conclusions, we must eliminate all differences of value and all differences of intensity. We can then see

which intervals give the greatest satisfaction to the sense of vision. The attempt to reach conclusions on the question of color-contrast, by comparing colors in different values and of different intensities, is perfectly futile.

The greatest possible interval in the color scale is, as I have said, the interval of 180°, the interval between opposite colors of the circle. These colors are known as complementaries. In the scale of six colors there are three pairs of complementaries: red and blue, purple and green, yellow and violet. For the sake of brevity we will indicate the colors by their initial letters: R for red; Y for yellow; G for green; V for violet; B for blue; P for purple; N for neutral. For the scale of neutral values we have already a terminology. Complementary colors, when tones of the same value and intensity are mixed together, neutralize one another, approximately. The relation of the complementary colors may, therefore, be stated in this form: —

```
Y — N — V
R — N — B
P — N — G
```

Observe that the complementaries balance, one against the other, on the intermediate neutral, when of the same value and intensity. The degree of intensity may be represented by the distance or space between the sign of the color and the sign of the neutral which separates it from its complementary. The greater this distance the greater the intensity. In the statement which follows, yellow and violet and purple and green are all equally intense, but the red and the blue are twice as intense: —

```
  Y — N — V
R —— N —— B
  P — N — G
```

The complementaries balance on the intermediate neutral, other things being equal, at equal distances from one another on the straight line connecting their centres. But in the arrangement

```
R — N —— B
```

the neutral being the ground-tone, the red being only half as intense as the blue, it will have to be moved to twice the distance, unless its

measure or quantity is doubled. I shall, presently, speak of measure as an element of balance.

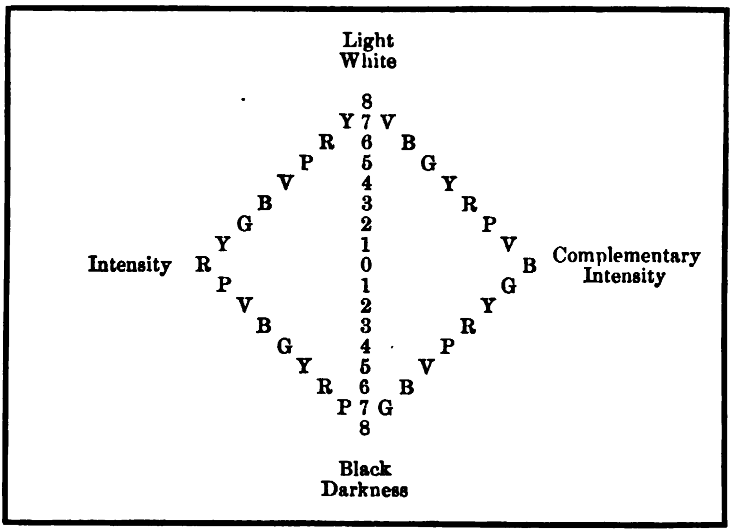
When it comes to the consideration of color intervals we have to think not only of the interval between one color and another in the spectrum scale, but, also, of the interval between each color and the neutral in which it disappears and is lost to vision. Take red, for example, in its greatest possible intensity, an intensity limited by the pigment material which we possess. This red is contrasted not only with its neighbors in the scale of colors, purple on the one hand and yellow on the other, but it is contrasted with itself in various degrees of neutralization. Establishing the greatest possible intensity of red on the one hand and a perfect neutrality on the other, both in the same value, and using for measure and for shape the circle of half an inch radius, make a scale of nine tones of red, the extremes of intensity and neutrality being included in the scale. What has been said of the other scales may be said of this one; a repetition is unnecessary.

We have considered the scale of values and the scale of colors separately. Now let us put the two scales together. The values being neutrals in every case, we can set complementary scales of colors on the right and left of the scale of values. That will give us two scales of colors, and between them the scale of values, as follows: —

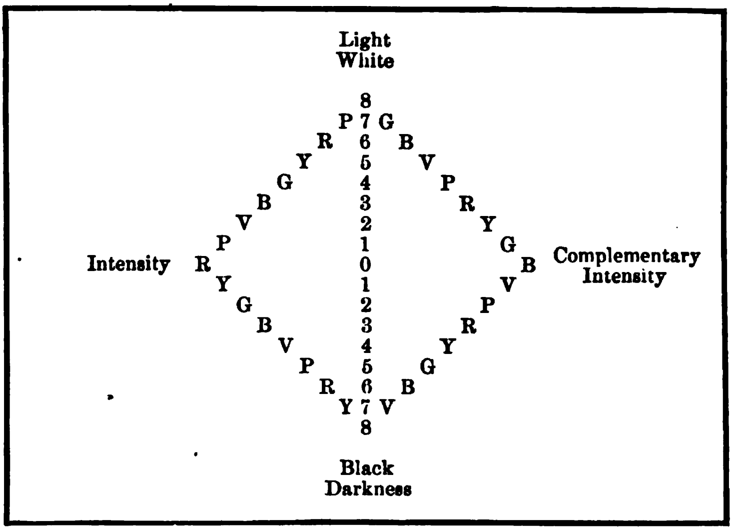
	Light White	
G	8	P
Y	7	V
R	6	B
P	5	G
V	4	Y
B	3	R
G	2	P
Y	1	V
R	0	B
P	1	G
V	2	Y
B	3	R
G	4	P
Y	5	V
R	6	B
P	7	G
V	8	Y
	Black Darkness	

Following this diagram, put in the place of the value numbers values of neutral color, moving from the central neutral up towards light (white)

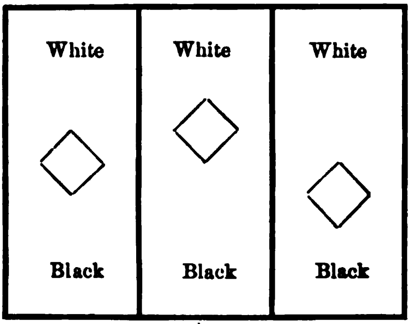
and down towards darkness (black). Then, on a ground-tone of the central neutral, alongside of the values and in the values, set the colors in spots of paint, all in the same intensity: if you can. You will immediately discover that you cannot do this. The colors in the light values are inevitably neutralized by white, and colors in the dark values are inevitably neutralized by black or some equivalent dark neutral. It is only towards the centre of the scale of values that you can get to any considerable intensity of color. If you consider the matter you will understand that this neutralization of the colors in light and in darkness is as it should be. It is exactly what happens to the colors in nature as they occur between light and darkness. Color is observed in its greatest intensity at the half-point between the light, whatever it is, and the darkness, whatever that is. It is evident that the form in which I have described the relation of the color and value scales needs to be modified. The colors as they approach the half-point between light and darkness must become more and more intense, the greatest possible intensity being reached at the half-point, exactly. We have seen how the measure of intensity can be indicated, diagramatically, by increasing or diminishing the space between the complementary colors in any value and the intermediate neutral; so all we have to do in order to describe the law of increasing and decreasing intensities is to pull the color scales apart at the half-point between the extremes of light and of darkness. This has been done in the diagram which follows: —



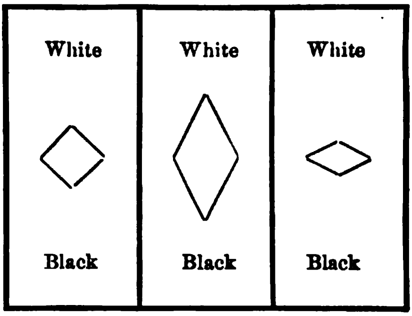
It will be found that this system works just as well if we turn it upside down. In doing this the relation of the color scales to the value scale is reversed, as in the following diagram: —



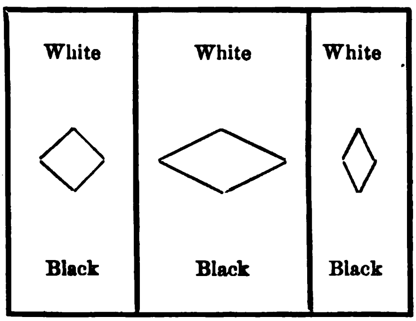
The diagrams which have been given show systems in which the colors red and blue are the dominant colors, having the greatest intensity. Predominance might be given to yellow and violet, or to purple and green, or we might bring the point of intensity between two pairs of complementaries. In that case we should have four colors as dominants, all equally intense. Every change of the dominants means, of course, a change of the whole system. The system may be changed in other ways. We can raise or lower its pitch within the extremes of white and black, thus: —



We can extend or contract the scale of values, thus: —



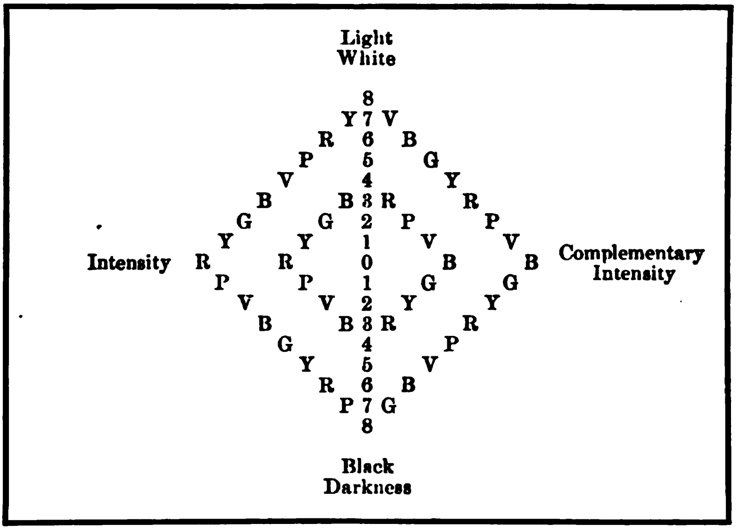
We can increase or diminish the degree of intensity, thus: —



By these various modifications an infinite number of specific forms of the system can be developed, all consistent with the system in its abstract idea.

If necessary, a system of half lights, half darks, and half intensities

of color can be used in connection with the one described, in the manner shown in the following diagram: —



As we increase the number and variety of tones to be kept all at equal intervals of equal contrasts, all in perfect rhythm and balance, the problem of consistency, which is the problem of art, becomes more and more difficult.

There is a possible objection to the system of color-values or tones which I have described. In the spectrum the colors are all equally intense. They differ only in value or luminosity. In the system just described this equality of intensity is ignored, and as to the luminosities, if they are observed on the hot side of the spectrum, they are ignored on the cold side, and if they are observed on the cold side they are ignored on the hot side. A different arrangement of values and colors is possible. If we distribute our range of light into five registers, — a register of half-tones, a register of lights, a register of darks, a register of high lights, and a register of extreme darks, — we can consider each one of these five registers as a potential spectrum, and we can arrange the colors in each register according to their several values or luminosities and have them all equally intense. The increase or diminution of intensities is not, then, from color to color but from register to register. In the scale of five registers, the middle one will be the register of greatest intensities. The registers above it and below it will be registers of less and of least intensity. This system is described in the following diagram: —

Light
White

Y N
G
High R N B Lights
P
V

Y N
Register of G
R N B
P Lights
N V

Y
Register of Half-Tones G
R
N B
P Intensities
N V

Y
Register of G
R N B
P Darks
N V

Y
G
Extreme R N B Darks
P
N V

Black
Darkness

This system would seem to be a particularly natural and proper arrangement of the values and the colors, for, if you throw the spectrum on white paper in sunlight the colors are seen all pale in the white light, equally intense so far as you can see them, but with the differences of value or luminosity which are indicated in the diagram. If you throw the spectrum on white paper in shadow (half light), you see the colors in equal intensity and in the greatest intensity, with the same differences of luminosity. If you throw the spectrum on black paper in shadow, you will observe the same equal intensity of colors, so far as you can see them, and the same differences of luminosity, but the whole spectrum is disappearing in neutral darkness. This system of color-values or tones

in which we have a spectrum to a register, in which the colors in each register are all equally intense, but in values representing their several natural luminosities, cannot, of course, be turned upside down, because that would reverse the luminosities; but the system admits of the other changes which I have described, — the changes of pitch, the extension or contraction of the value scale, and the extension or contraction of the intensities.

When it seems desirable, the middle register of greatest intensities may be left out of the system. The register of lights and the register of darks can then be brought close together, just above and just below the central neutral. Then the lights and the darks are all equally intense, and the first diminution of intensity is found in the register of high lights and in the register of extreme darks. This arrangement may be used both in Pure Design and in Representation. It is a system which ought to give great satisfaction to the colorist because of the number and variety of the colors, all equally intense, which it allows him to use.

If you take your palette and, following any of the diagrams which I have given, work out an illustration of the system, taking the central neutral as ground-tone, and putting the tones in circles of half an inch radius, you will observe that you have in the relationship of the tones a relation of balance, of rhythm, and of harmony. The system, whichever system it is and whatever form of the system is followed, is an illustration of Pure Design. Again, I am tempted to quote a passage of Plato in his Symposium (§ 187), in which the physician Eryximachus says that "harmony is composed of differing notes of higher or lower pitch which disagreed once but are now reconciled by art." In these various systems of color-values or tones, we have a reconciliation of many differing elements harmonized by the art of design. Observe how the rhythms of the different scales are so disposed that they balance in a perfect equilibrium, and how by the principle of equal intervals of equal contrasts the many elements of each system are all perfectly related.

Now we must take up and consider the second element of the spot of paint, — measure. In order to do this without confusion, take one tone, black on white paper, and one shape, the square. Thus eliminating all differences of tone and of shape, you can vary the measure and study it in all possible variations. Take some white paper and draw on it five black squares of different sizes. Observe that you have harmony of tones because the squares are all black, and you have harmony of shapes because the shapes are all square, but you have no harmony of measure. There is no connection between your measures, unless you have made

one, intentionally. It would not happen by accident. Now draw five squares in a scale, so that they shall be as 1 to 2, to 4, to 8, to 16, to 32, in the proportions of their measures. This is easily done by drawing the second on the diagonal of the first, the third on the diagonal of the second, and so on. Observe the difference between the five related and the five unrelated measures; the harmony of the related measures. Arrange the related measures in a row at equal intervals apart, the smallest first and the largest last, and observe how you have in your arrangement not only a harmony of measures which the scale-relationship gives, but you have, also, in the connection of the measures, a rhythmic relationship. The eye is led from measure to measure, just as it was led in the scale of values from value to value. By rearranging the rhythm of the measures, the movement can be made to change its direction and also its shape. By bringing the squares close together the movement becomes abrupt. Separating the squares by a larger interval, you can make the movement more gradual.

There is another point of view from which the measure must be considered. Every measure is a force of attraction, and the amount of this attraction is determined (other things being equal) by the measure itself. A large measure attracts more attention than a small one. The measure of two attracts twice as much attention as the measure of one. We have in our scale of measures, therefore, a scale of visual attractions proportioned as 1 to 2, to 4, to 8, to 16, to 32. Break up the scale and scatter the squares over your paper and observe that the eye is no longer led in a rhythm, but is held at rest by the opposition of attractions at the point which is their centre of equilibrium. When the problem is, to find this point, we must remember the law of balance: that equal attractions (measures in this case) balance at equal distances on a straight line connecting their centres, and that unequal attractions balance in the same way but at distances inversely proportional to them. In balancing tones we considered the element of contrast, measures being equal. In balancing measures we consider what they amount to respectively. The centre of equilibrium may be indicated by a point, or more satisfactorily by a symmetrical outline enclosing all the balanced measures and having with them a common centre. When the measures are accidental and unrelated, as they were before we brought them into scale-relationship, they are nevertheless attractions which hold the eye at their centre, and the centre can be found, approximately, by means of a small unit of measurement taken as a common divisor. The centre can be approximately ascertained by visual feeling, but we are talking about a scientific

basis for design, to be a verification or correction of visual feeling. The part which visual feeling plays in design is well enough understood.

The third element of the spot of paint, the one which we have not yet considered, is shape. To study shape alone we avoid all differences of tone and measure. For tone we may take black on white paper, and for measure the square of an inch. Then we must vary the shape in every possible way without varying either the tone or the measure. It is a little difficult to vary the shape without varying the measure, but we can do it, approximately, with the help of an underlay of small squares put under a tracing paper upon which we draw. The power of estimating the measure of the shape, no matter how irregular it is, is a power which every draughtsman, every painter, every designer must have. Make as many different shapes as you can, all black on white paper, and all in the measure of the square of an inch. Observe that some of the shapes are rhythmical, suggesting a joint action or movement of parts, that others are symmetrical, suggesting opposition or contradiction of parts, while others show both rhythmic and symmetric elements. Shapes are in harmony when they have the same or a similar character. Straight lines go together in harmony. Curved lines have in common their curvature, and fall into classes, circles, spirals, etc. Square spots harmonize as squares, and round spots as rounds. Angles go together in scale-relations based upon degrees.

Observe, however, in this connection as in others, that a little difference is more disturbing than a large difference, when there is no sufficient reason for any difference at all, when the repetition of the same shape-character would be as satisfactory. Most perfect harmony exists, of course, between shapes which have one and the same character, so in design we prefer a repetition of similar elements to any composition of insignificant differences. We are, however, apt to have differences of character given to us in the terms or conditions of our problem. What we have to do is to make the best of these conditions. In such cases we can make up for any lack of harmony in shapes by harmony in other than shape-relations. Shapes are in harmony when they have the same measure (harmony of measure). They are in harmony when they have the same tone (harmony of tone). They may have the same value without having the same color, and the same color without having the same value. They may have the same color without having the same intensity, so that there are many ways of achieving harmony when there is no harmony of the shapes themselves.

Shapes having the same measure are in balance when they are reversed

and set side by side so as to contradict one another. A perfect balance or antithesis of shapes is what we call symmetry. Symmetry is, accordingly, a specific form of balance. It is shape-balance, and as such it must be distinguished from tone-balance and measure-balance. The only perfect balance of shapes is the balance of similar shapes set in reverse, one against the other, and having the same measure; but we may have a partial balance in the reversion and opposition of similar shapes when they have different measures.

When two or more shapes are arranged so as to suggest a joint action or movement, we have what may be called a rhythm of shapes. This rhythm may be straight or curved in its character, or it may combine both curvature and straightness. As the eye moves more rapidly upon a straight line than upon any other, a rhythm showing many straight lines, all having the same direction, will give to the eye the sense of rapid movement, and this sense of rapid movement is lost in a rhythm which shows many curves or angles upon which the eye moves more intricately and therefore more slowly. There is another element to be considered in connection with the rhythmic composition of shapes; that is the suggestion of a possible resistance. The idea of resistance does not lie in the shape of the spot of paint, in the shape itself, but in a mental association. If we wish to produce the sense of rapid motion we must be sure not to suggest any opposition or resistance. Rhythms set in contrary motion tend to balance one another, and in the measure in which they balance one another they bring the eye to the rest of equilibrium.

I have now described the spot of paint in its three elements, tone, measure, and shape, and I have shown, or tried to show, how each of these elements may follow the principles of balance, of rhythm, and of harmony, which, as we have seen, are principles of order and of beauty. In the practice of Pure Design, which is the composition of spots of paint for the sake of order and beauty, we begin with a few tones, measures, and shapes, and try to bring them into the relations of balance, rhythm, and harmony; in other words, into an idea of beauty. When we have achieved this, in the composition of a few elements, we do the same thing with a larger number, proceeding, thus, from comparatively simple to more and more difficult problems. The elements which we use in any problem are not necessarily simple. We may take simple tones, measures, and shapes, or we may take compositions of them. Then the problem takes the form of a composition of compositions. In order to rise to anything important in design, the designer must be able to think freely and easily

in the terms of his art. The designer must be able to think in tones, measures, and shapes precisely as the composer of music thinks in the sounds of voices and of instruments. The measure of his ability as a designer is then revealed in his power to think of many things in single ideas, and to express in single ideas many things. At first a somewhat painful effort has to be made to bring the composition of tones and measures and shapes into the lawful relationship of a single idea; but, by degrees, the designer comes to think of his tones, measures, and shapes in lawful forms only. He is then a master, and he will follow the suggestions of his imagination as it leads him into the world of tone-, measure-, and shape-ideas. This world must be as wonderful as the world of musical sounds. We know something of that in the revelations which the great composers of music have given us in their compositions. Of the possibilities of Pure Design, we can only guess what they may be. Then, when it comes to Design in Representation, and we have in addition the lawful composition of tones, measures, and shapes, the expression of visual knowledge in the form of true ideas, we rise to still higher possibilities in the connection and relationship of Beauty with Truth. As we rise above the accidents of vision or of memory to the knowledge of things seen in their ideas or ideals, we discover that our knowledge of nature or life is a knowledge of Nature's consistency, of her balances, her rhythms, her harmonies, her order, her incomparable beauty. In other words, as science rises from particulars to what is general and universal, as she rises to the understanding of principles and laws, causes and sequences, she comes to a conception of nature as pure design. The statement of scientific truth becomes an illustration of pure design, and art and science become one. "At last the vision is revealed to him of a single science, which is the science of beauty everywhere." (Plato, Symposium, § 210.)

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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY
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THE OCCLUSION OF MAGNESIC OXALATE BY CALCIC OXALATE, AND THE SOLUBILITY OF CALCIC OXALATE.

BY THEODORE W. RICHARDS, CHARLES F. MCCAFFREY, AND HAROLD BISBEE.

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FOR many years it has been known that magnesic oxalate is carried down with calcic oxalate in the ordinary course of quantitative analysis. This is only one case of the very general phenomenon of concomitant precipitation, or occlusion, sometimes explained with the help of van't Hoff's conception of "solid solution," * and not widely understood, no matter what name may be used. It is of considerable interest, both practically and theoretically, to obtain evidence concerning the mechanism of this class of analytical irregularities.

In a foregoing paper,† one of us has shown that occlusion is probably the distribution of an *undissociated* substance between the solution and the nascent solid. If this is the case, the amount of material occluded should be directly proportional to the concentration of the undissociated part of the substance in question. The application of this idea to the present case of calcium and magnesium seemed capable of furnishing a further clue to the theory of the general problem, as well as of providing a more satisfactory analytical method in this particular case. Since the magnesium comes down with the calcium in the form of oxalate, it is the concentration of the *undissociated magnesium oxalate* in the solution which will determine the amount of the occlusion, if this hypothesis be true. According to the law of mass action and the dissociation hypothesis, this concentration may be increased by adding either constituent ion in excess. It may be diminished by adding a large excess of any other partially ionized substance,‡ especially those

* Schneider, Z. phys. Chem. **10**, 425 (1892).

† Richards, These Proceedings, **35**, 377 (1900).

‡ Compare Arrhenius, Z. phys. Chem. **31**, 198 (1899).

which form a complex ion or undissociated substance in solution involving either magnesium or oxalic acid.

One of the most effective causes diminishing the concentration of the magnesic oxalate, and therefore the occlusion, should be the hydrogen ion, for this tends to remove the oxalic ion, and hence to cause the ionization of undissociated magnesic oxalate.

Another effective cause should be an increase in the concentration of ammonic salts present, which not only exert the effect of any other partially dissociated salts, but have also the well-known property of forming complex compounds with magnesium. This formation naturally removes magnesic ions and hence magnesic oxalate from the solution.

A third obvious means of diminishing the concentration of the magnesic oxalate is by diluting the solution. By this process, the actual amount of undissociated oxalate is diminished, and the concentration of the undissociated part is thus diminished even more rapidly than in the ratio of the changing volumes. All of these tendencies except the second apply to the calcium as well as to the magnesium, although to a less extent, for calcic oxalate is far less soluble than magnesic oxalate. Calcium has not so great a tendency to form complexes with ammonic salts as magnesium.

These relations are partially expressed by the following scheme, in which no attempt is made to express the exact nature or the ionization of the magnes-ammonium complex: —

$$
\begin{array}{cc|ccccc}
MgCl_2 & \rightleftarrows & 2Cl^- & + & Mg^{++} & & \\
+ & & + & & + & & \\
x\,NH_4Cl & & 2H^+ & + & C_2O_4^{=} & \rightleftarrows & H_2C_2O_4 \\
\uparrow\downarrow & & \uparrow\downarrow & & \uparrow\downarrow & & \\
Mg(NH_4)_xCl_{x+2}(?) & & 2HCl & & MgC_2O_4 & \text{in solution} & \\
 & & & & \uparrow\downarrow & & \\
 & & & & \boxed{MgC_2O_4 + CaC_2O_4} & & \\
 & & & & \text{Precipitate} & &
\end{array}
$$

Reviewing the older work upon this subject, one finds that most of the known facts support the hypothesis. Fresenius, in the few experiments which are recorded in the end of the second volume of his "Quantitative Analysis," * showed that the weight of the calcic precipitate obtained was less when the dilution was greater; that it was

* Fresenius, Quantitative Analyse, 2, 821 (1877–1887).

diminished by the presence of an excess of either ammonic hydrate or ammonic chloride. When acetic acid was present, too little precipitate was obtained, and a very large excess of oxalate in alkaline solutions gave too much precipitate. But Fresenius attacked the problem merely in an empirical fashion; the guiding hypothesis of the present day had not yet been suggested. It did not occur to him to study the effect of gradual precipitation in a strongly acid solution.

Most writers of handbooks upon quantitative analysis have accepted Fresenius's method of double precipitation, and the recent literature upon the subject is unusually scanty. In a paper, of which we have seen only an abstract,* Hefelmann calls attention to the necessity of using dilute solutions in order to attain satisfactory results; but other important references to the subject in periodical literature could not be found. A good method devised by H. P. Talbot, not to be found in the periodicals, will be mentioned later.

For our experiments calcic chloride and magnesic chloride or sulphate were prepared separately in a state of great purity. By the repeated crystallization of the nitrate, the calcium material was freed from its usual impurities, and the carbonate was precipitated from this nitrate by means of pure ammonic carbonate. Standard solutions of this material in hydrochloric acid were made from time to time, and the concentration of these solutions was determined with the utmost care by precipitation with ammonic oxalate, according to the method to be described. Magnesic chloride and sulphate were carefully purified by repeated crystallization, and experimental proof was obtained of the absence of calcium from them. The magnesium solutions were always of a strength approximately equivalent to the calcium. Ammonic chloride was made by passing pure ammonia gas into freshly made hydrochloric acid; oxalic acid was especially purified; and all the ammonia used was freshly prepared in platinum vessels.

In the first place, the worst possible results were obtained in order to show how great an improvement was possible by the successive introduction of the modifications suggested above. To neutral solutions of a mixture of 25 c.c. each of the magnesium and calcium solutions, made up to 200 c.c., was added an excess of ammonic oxalate, but without the addition of either ammonic chloride or acid. The two precipitates thus formed were ignited at a very high temperature until constant in weight. Below are recorded the results: —

* Zeitschr. anorg. Chem. 18, 401 (1898).

PRECIPITATION IN ABSENCE OF PRECAUTION.

No. of Experiment.	Wt. of Ignited Precipitate.	Wt. of CaO taken (determined in Parallel Portions).	Difference. MgO present.	Error.
1	0.2743	0.2358	0.0385	+ 16.4%
2	0.2597	0.2358	0.0239	+ 10.1%
			Average error,	+ 13.3%

The next step was to test the effect of hydrochloric acid — or rather of the concentration of ionized hydrogen — upon the occlusion. Since in this case from an acid solution all of the calcium could not be precipitated, a larger amount was used, but the concentration of the magnesium was the same as before. 25 c.c. of the magnesium solution, 75 c.c. of the calcium solution, and 10 c.c. of normal hydrochloric acid were diluted up to 200 c.c. To this solution, heated to boiling, were added 27 c.c. of normal oxalic acid, to which had previously been added 10 c.c. of normal hydrochloric acid for the sake of diminishing its dissociation. Over half of the calcium was precipitated in the form of fine white crystals of the oxalate. It is well known that the substances most capable of easy supersaturation are those which form the largest crystals; and conditions which tend to promote the solubility of a precipitate in general tend to promote its ease of supersaturation. Hence precipitates formed from solutions in which they are somewhat soluble, are more crystalline than those formed from liquids in which they are insoluble. Calcic oxalate is no exception to this general rule. The easily handled precipitate was collected, thoroughly washed, ignited to constant weight at a bright yellow heat, dissolved, reprecipitated, re-ignited, and weighed again. The results below show how comparatively small was the occlusion of magnesium in this precipitate.

PRECIPITATION FROM ACID SOLUTIONS.

No. of Experiment.	Weight of First Oxides.	Weight of CaO (2d).	MgO present.	Error.
3	0.4136	0.4100	0.0036	0.88%
4	0.4128	0.4087	0.0041	1.00%
			Average error,	0.94%

The average error attained only one-fourteenth of its previous magnitude. Thus the presence of acid has a remarkable restraining effect upon the occlusion; a fact in accordance with the prediction of the theory.

In the next place, the action of ammonic chloride was studied. A neutral solution of 25 c.c. each of the calcium and magnesium solutions was made up to 200 c.c. and treated with two grams of ammonic chloride and the same amount of ammonic oxalate as in the first experiment. Two trials of this process yielded the following results: —

THE EFFECT OF AMMONIC CHLORIDE.

No. of Experiment.	Weight of Oxides found.	Weight of CaO taken.	MgO present.	Apparent Error.
5	0.2376	0.2358	0.0018	0.77 %
6	0 2364	0 2358	0.0006	0.25 %
			Average error,	0.51 %

About 1.1 milligrams more of calcic oxide was recovered from each of these solutions by the addition of much more ammonic oxalate. This precipitate, which fell after some time, was redissolved and reprecipitated before weighing in order to free it from magnesium. The total amount of magnesic oxide in the first precipitate was thus about one per cent, or somewhat more than in the precipitates from an acid solution.

These experiments show that ammonic chloride diminishes very much the tendency of the magnesic oxalate to be precipitated, but that it exerts also a similar although much less considerable effect upon the calcic oxalate. The more ammonic chloride is added, the greater concentration of oxalate ion is necessary completely to precipitate the calcium, but the more effective is the retention of the magnesium in the solution. The limit to the advisable amount of ammonic chloride depends upon the subsequent method to be used for the determination of the magnesium; but for ordinary purposes an equivalent-concentration ten times as great as that of the magnesium present should answer.

This action may be explained, as has already been stated, partly by an effect which would be caused by any electrolyte and partly by the additional formation of an unstable complex. The existence of this complex is abundantly confirmed by the other reactions of magnesium in the presence of a large amount of ammonic chloride. It is well known that many of the common reactions fail, and that other reactions, such

as the precipitation of ammonic magnesic phosphate, require more time for their completion, when much ammonic chloride is present.*

If, as a matter of fact, the occlusion is proportional to the concentration of the undissociated magnesic oxalate, additional ammonic oxalate, even in the presence of ammonic chloride, ought to increase the weight of the precipitate. The following experiments, similar to the last except that in each case three grams instead of one of ammonic oxalate were used, were made to test this point.

THE EFFECT OF EXCESS OF AMMONIC OXALATE.

No. of Experiment.	Weight of Oxides.	Weight of CaO taken.	MgO present.	Error.
7	0.2390	0.2358	0.0032	1.36%
8	0.2393	0.2358	0.0035	1.48%
			Average error,	1.42%

Thus a trebling of the amount of oxalate present increased the error by about a third of its previous value. At first one is surprised that the increase is not greater; but it must be remembered that the oxalate was added rather slowly, so that most of the precipitate was formed before a large excess of oxalate was present. It is chiefly the *concentration of the magnesic oxalate present at the instant of precipitation*, not the subsequent amount in contact with the precipitate, which influences the distribution. When the precipitate has once appeared as a solid, the action must be confined to the surface; for diffusion into solids is exceedingly slow because of their rigid structure.

A number of analyses were made in the hope of combining all the circumstances which tend toward complete separation, and of eliminating all those which oppose it; but yet further difficulties arose. It seemed probable that by *gradual* neutralization of an acid solution the calcic oxalate might be precipitated in an environment containing as little magnesic oxalate as possible, and thus be as free as possible from this impurity. The mode of procedure was as follows. To a mixture containing in 200 c.c., 25 c.c. each of the calcic and magnesic solutions, were added three grams of ammonic chloride, 1.6 grams of oxalic acid, and enough

* Compare Ostwald, Scientific Foundations of Analytical Chemistry (Macmillan, 1895), p. 136.

hydrochloric acid to keep the calcic oxalate in solution. Subsequently strong ammonia was poured very slowly into the liquid, with continual stirring, until the solution contained an excess of ammonia. Methyl orange was found to assist materially the exact neutralization.

PRECIPITATION BY CONCENTRATED AMMONIA.

No. of Experiment.	Weight of Mixed Oxides.	Weight of CaO taken.	Weight of MgO.	Error.
9	0.2373		0.0015	0.6%
10	0.2383	0.2358	0.0025	1.1%
11	0.2384		0.0026	1.1%
12	0.2387		0.0029	1.2%
			Average error,	1.0%

Some calcium was found in the mother liquors upon the addition of more ammonic oxalate; but this is included above. Evidently no material gain in accuracy is effected in this series, and the reason is not hard to find. The ammonia was so strong that it caused instant neutralization of the acid in its neighborhood; and hence the idea of the method was defeated, for the design was to effect a *gradual* neutralization, giving time for the supersaturated calcic oxalate to separate.

In the next series twice as much oxalic acid was used, but the ammonia added to effect the precipitation was far less concentrated.

PRECIPITATION BY DILUTE AMMONIA.

No. of Experiment.	Weight of Mixed Oxides.	Weight of CaO taken.	Weight of MgO.	Error.
13	0.2375		0.0017	0.7%
14	0.2374		0.0016	0.7%
15	0.2369	0.2358	0.0011	0.5%
16	0.2380		0.0022	0.9%
17	0.2379		0.0021	0.9%
			Average error,	0.74%

Thus, diluting the ammonia had the beneficial effect which was expected. In the presence of so much oxalate the solution was, of course, practically free from calcium, hence this result indicates a distinct improvement.

It has been already noticed that dilution of the original solution has been found by others to lessen the amount of magnesium carried down. This fact might have been easily predicted by the hypothesis that the phenomenon is regulated by the Distribution Law. It is further verified by two experiments given below, in which the method of Experiments 13–17 was repeated, except that the volume was 800 c.c. instead of 200 c.c.

THE EFFECT OF DILUTION.

No. of Experiment.	Weight of Mixed Oxides.	Weight of CaO taken.	Weight of MgO.	Error.
18	0.2369	0.2358	0.0011	0.42%
19	0.2371	0.2358	0.0013	0.54%
			Average error,	0.48%

Here also no calcium could be recovered from the mother liquor, hence it is clear that the dilution was really of service, reducing the magnesic oxide from 0.74 per cent to 0.48 per cent. The theoretical diminution to less than a quarter of the former value was not to have been expected, for the addition of the ammonia in finite dilution introduces an irregularity for which it is impossible to make quantitative correction.

At this stage in the work it was found that a method of precipitation essentially identical with that just given had already been published by Professor H. P. Talbot in his admirable treatise on the elements of Quantitative Analysis.* So far as we know, no account of it is to be found elsewhere. Since no examples accompany this publication, the preceding work, which was wholly independent, affords useful confirmation of his method as an approximate one for rapid work.

The chief difference between the method of Talbot and ours lay in the respective amounts of oxalate, a much larger amount having been used in our work in order to insure the total precipitation of the calcium.

It is clear from the above account that this large initial excess of the

* Talbot, Quantitative Analysis (Macmillan), 3d ed. p. 42 (1899).

oxalate, although necessary so far as the calcium is concerned, must increase the amount of precipitated magnesium oxalate. But according to our original hypothesis, this excess is chiefly harmful when it is present at *the moment of precipitation*, although it is not really needed to prevent the solution of traces of calcic oxalate until the precipitation is practically finished. Hence the oxalic acid also should be added gradually, or at least in two portions, the first to supply enough oxalate to combine with the bulk of the calcium, and the second to diminish the solubility of the last traces. This plan was followed in the following work.

Another point was as yet undecided, — the length of time needed for the essentially complete separation of the calcium. Hence five determinations similar to the above were made with solutions each capable of yielding 0.1496 grams of lime and an equivalent quantity of magnesia. The only variation in these experiments was in the time elapsing between precipitation and filtration.

THE EFFECT OF THE TIME BETWEEN PRECIPITATION AND FILTRATION.

No. of Experiment.		Weight of Precipitate.	Error.
20	Filtered after standing $\frac{1}{2}$ hour	0.1488	− 0.53 %
21	" " " $\frac{3}{4}$ hour	0.1492	− 0.27 %
22	" " " 24 hours	0.1501	+ 0.33 %
23	" " " 48 hours	0.1507	+ 0.73 %
24	" " " 80 hours	0.1511	+ 1.00 %
	Amount of calcic oxide present,	0.1496	

The filtrates from the first two of these (Nos. 20 and 21) deposited traces of calcic oxalate on standing for two hours, but the others did not deposit a trace in several days. From these five experiments two conclusions may be drawn: first, that several hours are needed for a separation of the last weighable traces of calcium, even when much ammonic oxalate is used; and secondly, that after the calcium has all been precipitated, magnesium oxalate is absorbed by the precipitate at a fairly constant although very slow rate, from a solution which will of itself deposit no solid. The magnesic oxalate is slowly occluded by

the precipitate or deposited upon it even after the precipitation of the calcium salt.

This points to another flaw in the earlier work, — namely, the solutions, which had all been allowed to stand for at least sixteen hours before filtering, had been left too long in contact with their precipitates.

In a case of this kind great accuracy is to be obtained only by a succession of approximations; hence it seemed worth while again to make a series of precise analyses, embodying all the advantages which had been found up to this point, in order to discover from their possible variations if there might be still another cause of error as yet undetected.

Newly prepared very pure solutions were used in these analyses, which were made two years after the ones previously detailed. All the precautions suggested by the foregoing pages were heeded, and two series of results were obtained, one from calcium solutions only, and the other from solutions containing precisely the same amount of calcium with an equivalent amount of magnesium. These are given below in parallel columns: —

PRECIPITATION OF PURE CALCIC OXALATE.
(Volume at precipitation = 200 c.c.)

No. of Analysis.	Time of Digestion.	Weight of CaO.
25	3.5 hours	0.3063
26	3.5 "	0.3064
27	3.5 "	0.3065
28	3.5 "	0.3064
	Average,	0.3064

PRECIPITATION OF CALCIUM IN PRESENCE OF MAGNESIUM.
(Volume at precipitation = 500 c.c.)

No. of Analysis.	Time of Digestion.	Weight of CaO.
29	2.5 hours	0.3060
30	2.5 "	0.3060
31	3.5 "	0.3064
32	3.5 "	0.3066
33	3.5 "	0.3058
	Average of last three,	0.3063

The agreement between the two averages is very striking; it is to some extent due to a compensation of errors. Even when we have made due allowance for these, however, it furnishes strong evidence in favor of the hypothesis which led to the before mentioned precautions. Experiments 29 and 30, not included in the average, show that at the

end of two hours and a half there probably still remained a trace of calcium in the solution.

While the possibility of separating calcium from magnesium with considerable completeness by a single operation had thus been demonstrated, one point still remained to be studied. In the course of the washing of these precipitates of calcic oxalate, it was noticed that the wash-waters always gave a faint opalescence with neutral argentic nitrate, an opalescence which dissolved in nitric acid. Unlimited washing seemed not to free the precipitate from this substance, hence the substance must have been calcic oxalate itself. In short, calcic oxalate appeared to be soluble in boiling water to an extent sufficient to affect a precise analysis. Since no account of accurate determinations of the solubility of calcic oxalate in boiling water could be found, the next problem was to determine this solubility.

The calcic oxalate was precipitated in the usual manner and washed with exceeding thoroughness. A solution, not necessarily saturated, but closely resembling one which might be obtained in the process of washing, was made by stirring the powder for fifteen minutes with water in a platinum dish kept at the desired temperature. Of the three usual methods of analyzing such a solution, — by weighing, titration, and the measurement of electrical conductivity, — volumetric determination

SOLUBILITY OF CALCIC OXALATE. SERIES I.

	Temperature = 90°.		
No. of Analysis.	Volume of Permanganate required by 100 c.c. of Sol.	Weight of Calcic Oxalate corresponding.	Remarks.
34	1.86 c.c.	0.00115	Fresh filter, thoroughly moistened.
35	1.81 c.c.	0.00112	Same filter as above.
36	1.81 c.c.	0.00112	Same filter as above.
	Temperature = 25°.		
37	1.10 c.c.	0.00068	Fresh filter.
38	1.06 c.c.	0.00066	Same filter as preceding.

seemed the best suited to the present purpose. The filtered solution was therefore titrated with a solution of approximately hundredth normal permanganate, of which one cubic centimeter corresponded to 0.00062 gram of calcic oxalate. The amount of the solution, 0.12 c.c., which was required to impart the usual pale pink color to the assay, was always subtracted from the total volume run out. In each analysis exactly a decilitre of calcic oxalate solution was used.

These results are typical of a number of similar determinations which were made in this way. The first portions running through a filter paper always seemed to contain slightly more calcic oxalate than the later portions, probably owing to the escape of fine particles which are retained by the filter when it has become somewhat clogged. The later values are probably the more reliable, hence it is clear that hot water will dissolve easily over a centigram per litre of calcic oxalate, while water at the ordinary temperature dissolves nearly seven milligrams per litre.

This solubility is altogether too great to be passed without heed in precise work. Its magnitude was such as to make desirable a more exact determination of a more nearly saturated solution.

The first problem to be solved in this connection was the retention of even the finest particles. The best filter papers of Schleicher and Schüll, Dreverhoff, and others were tested, all with the result already described; namely, that the first filtrate always yielded slightly more calcic oxalate than the following ones. Finally it was decided to use four layers of paper, and to reject at least half a litre of filtrate before beginning to collect for analysis. The filtration was effected by means of a platinum inverted filter devised by J. P. Cooke,* and a simple arrangement of tubes and stopcocks made the rejection of the first and the collection of the subsequent portions of filtrate an easy matter. The filtered liquid appeared perfectly clear on inspection in strong light. The inverted filter made it possible to maintain the filtering liquid at the desired temperature. The time of digestion at the higher temperatures was an hour; but at 25° an hour and a half was allowed. A very large platinum dish served as the vessel for digestion, and the liquid was suitably protected from the products of combustion of illuminating gas and other impurities. A diagram of the apparatus will furnish all further necessary explanation. As before, a hundred cubic centimeters of the solution served for each titration.

* These Proceedings, **12**, 124 (1876).

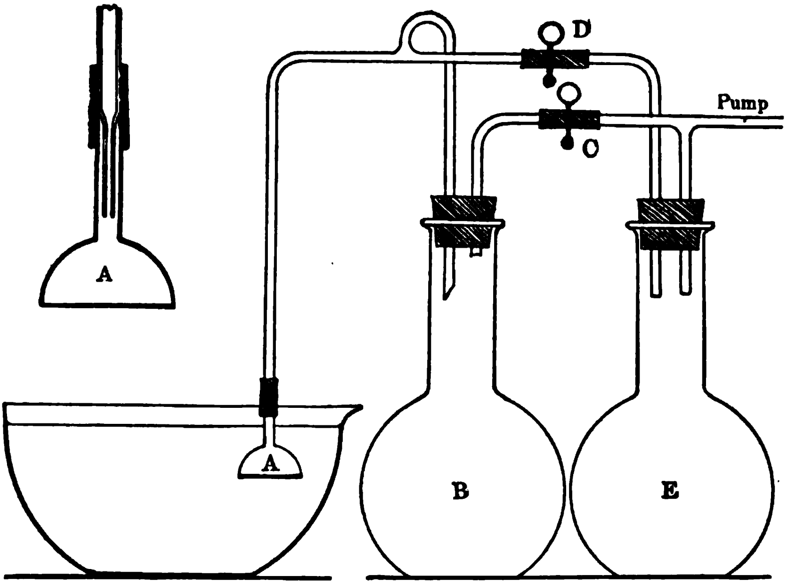

FIGURE I. APPARATUS FOR FILTERING.

A is the inverted filter, clad four-fold with filter paper. B is the collecting flask, which fills only when C is open and D closed. E serves to retain the rejected liquid.

It is not certain that these solutions were wholly saturated; but the difference in concentration between these and the earlier solutions, which had been digested during much less time, made it highly probable that any error from this cause would be less than the necessary errors of titration. Hence no further determinations were made.

After these determinations were finished, Kohlrausch and Rose's * determinations by means of electrical conductivity at lower temperatures were consulted, and were found to furnish agreeable confirmation of these independently obtained results. At 18° Kohlrausch and Rose's figure was 5.9 milligrams per litre, while our extrapolated value is 6.0 milligrams; and at 40° the respective figures are 8.0 and 8.4 milligrams. Our slightly larger values may be due to the fact that we determined all the calcic oxalate in solution, while Kohlrausch and Rose measured only that part which is dissociated. According to the table upon page 200

* Zeitschr. für phys. Chem., **12**, 234 (1890).

SOLUBILITY OF CALCIC OXALATE. SERIES II.

Temperature = 95°.

No. of Analysis.	Volume of Permanganate required by 100 c.c. Sol.	Weight of CaC_2O_4 in 100 c.c. Solution.
39	2.19 c.c.	0.00136 gram.
40	2.18 "	0.00135 "
41	2.35 "	0.00146 "
42	2.28 "	0.00141 "
	Average,	0.00140 gram.
	Temperature = 50°.	
43	1.55 c.c.	0.00096 gram.
44	1.56 "	0.00097 "
45	1.53 "	0.00095 "
46	1.52 "	0.00094 "
	Average,	0.000955 gram.
	Temperature = 25°.	
47	1.09 c.c.	0.00068 gram.
48	1.11 "	0.00069 "
49	1.08 "	0.00067 "
	Average,	0.00068 gram.

of Kohlrausch and Holborn's book (1898) this interpretation might account for the difference, but in any case they make no pretensions to great accuracy. In view of Ostwald's recent work on the surface tension of solids,* a more precise determination than ours would be of no service unless the diameters and shapes of the solid particles were defined.

* Ostwald's Zeitschr phys. Chem., **34**, 495 (1900).

In the light of all these facts, there can be no question that calcic oxalate is soluble enough to demand further precautions in washing than are usually taken. The obvious means of diminishing this solubility is to wash the precipitate with a dilute solution of ammonic oxalate, instead of with pure water. With the idea of testing the efficacy of this precaution, as well as with the purpose of determining the strength of a new solution of calcic chloride, the following series were made.

In the first place three portions, removed with a very exact 25 c.c. pipette, were individually precipitated by degrees in our usual fashion from a solution having a volume of two hundred cubic centimeters. They were each allowed to remain four hours before filtering. The weights of calcic oxide resulting upon ignition to constant weight at a bright yellow heat were respectively 0.3479, 0.3480, and 0.3480 gram. The last two of these were now dissolved in hydrochloric acid and reprecipitated with the utmost care by means of ammonic oxalate. The weights were now, after ignition, 0.3474 and 0.3475 gram respectively — an average loss of 0.00055 gram or 0.16 per cent. If pure water had been used for washing, the loss would have been much greater. This loss may have been due to incomplete precipitation, or to a slight solubility in the wash-water in spite of the presence of ammonic oxalate, or to the mechanical passage of exceedingly small particles through the filter. Whatever may be the cause, this deficiency is clearly a quantity which must apply to most if not all of the foregoing work. Its application does not cause sufficient change in the results to affect the conclusions which have been drawn; in many cases of comparison each of the numbers compared is affected equally.

It became now an interesting question to carry out in the presence of magnesium the operations just described. Except for the degree of dilution, the other conditions were in every respect like those named. In two experiments where the precipitation took place in a volume of 300 c.c., the weights of impure calcic oxide were respectively 0.3491 and 0.3489 gram, a gain of a milligram, or 0.29 per cent. In two other cases where the volume was 600 c.c., the weights were 0.3486 and 0.3483 gram respectively, a gain of 0.13 per cent.

This last gain is almost exactly equal to the inevitable loss during filtration, so that the occluded magnesia almost exactly replaced the lime which is not collected.

The slightly impure specimens of lime of the last two experiments, weighing respectively 0.3486 and 0.3483 gram, were now dissolved and reprecipitated as oxalate, which was washed with ammonic oxalate as

before. The resulting specimens of oxide weighed respectively 0.3469 and 0.3474 gram, an average of 0.34715 gram, while the weights obtained by a similar double precipitation in the absence of magnesium averaged 0.34745 gram, or 0.3 milligram more. This difference is too small to have much significance, hence the conclusion is allowable that as much of the lime as is practicable had been precipitated.

It is clear from these experiments that the double precipitation usually practised, while certainly eliminating the magnesium, inevitably involves the loss of calcium. The single precipitation minimizes this last risk, and by the compensation of two errors very small in themselves, gives a result which is very near the truth.

The conclusions attained in this paper may be summarized as follows: —

1. All those conditions which tend to diminish the amount of undissociated magnesic oxalate in a solution tend to diminish the amount of this impurity in calcic oxalate precipitated from the solution.

2. Hence evidence is furnished supporting the hypothesis that occlusion is a distribution of an undissociated substance between the liquid and the "nascent" solid phase.

3. Magnesic oxalate is precipitated upon the calcic oxalate after this is deposited, although far more slowly than while it is being deposited. For this reason the filtration should not be too long delayed.

4. Calcic oxalate is sufficiently soluble in pure water to cause grave inaccuracies in precise quantitative work.

5. This solubility may be diminished, but not wholly prevented, by an excess of ammonic oxalate in the wash water.

6. By heeding all these relations, a reasonably precise separation of magnesium and calcium may be made in a single precipitation. The details are as follows: The magnesium in the solution should be not much stronger than fiftieth normal. About ten times the equivalent amount of ammonic chloride, and enough oxalic acid to combine with all the calcium, should be added to the mixed solution. It is well to diminish the dissociation of the oxalic acid beforehand by the addition of two or three times its equivalent amount of hydrochloric acid. To the boiling mixture, colored with a drop of methyl orange, should be added slowly a very dilute solution of ammonia, with continual stirring and occasional pauses. The final stages of neutralization should not be reached in less than half an hour.

When the neutralization has been effected, a very large excess of ammonic oxalate should be added, and the mixture should be allowed to

stand for four hours. The precipitated calcic oxalate should be thoroughly washed with water containing ammonic oxalate. The filtrate will contain all but about 0.1 or 0.2 per cent of the magnesium, and the precipitate will contain all but about the same proportion of the calcium.

7. The precipitate, having been formed slowly from a solution in which it was somewhat soluble, is distinctly crystalline and far more easily handled than if it had been suddenly precipitated. This is a general effect, which might render service in other cases.

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CONTRIBUTIONS FROM THE CRYPTOGAMIC LABORATORY OF HARVARD UNIVERSITY. — XLV.

PRELIMINARY DIAGNOSES OF NEW SPECIES OF LABOULBENIACEAE. — III.

BY ROLAND THAXTER.

CONTRIBUTIONS FROM THE CRYPTOGAMIC LABORATORY OF HARVARD UNIVERSITY. — XLV.

PRELIMINARY DIAGNOSES OF NEW SPECIES OF LABOULBENIACEAE. — III.

By Roland Thaxter.

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During the summer of 1900 I took occasion to visit Berlin in order to examine the collections of insects at the Museum of Natural History there in search of Laboulbeniaceae, and through the courtesy of the director, Professor Moebius, and of the staff of the Entomological Laboratories, to whom I desire in this connection to express my great obligations, was successful in obtaining numerous new and interesting forms from all parts of the world. To the great kindness of Dr. David Sharp of Cambridge, England, I am further indebted for the privilege of examining, for a similar purpose, his magnificent collections, especially of Staphylinidae and Gyrinidae, as well as the large series of singular Carabidae brought from the Hawaiian Islands by Mr. Perkins. A considerable number of new or peculiar forms have moreover been added to the American flora since my return, for a portion of which I am indebted to Mr. Charles Bullard, who has very kindly placed his material at my disposal. The number of new forms from all sources thus combines to make a notable addition to the family as a whole, and indicates that my former estimates of its numerical importance were by no means exaggerated.

Among the most interesting of these novelties are those which have been derived from dipterous insects, since they not only enlarge our systematic knowledge of new or little known genera, but illustrate in a striking manner the curiously variable relation of these parasites to such soft-bodied hosts. That so considerable a number of species were found on Diptera is in a great measure due to Professor Dahl, who called my attention to the fact that some of the small flies collected by him at Ralum in New Pomerania, near New Guinea, were parasitized, and I was thus led to make a careful examination of the whole collection

with the results hereafter indicated. These dipterous parasites alone are included in the present paper; but descriptions of the remaining novelties will be published shortly. A set of duplicate preparations of all the material found at Berlin has been made, and will be deposited there as soon as the illustrations for the Supplement to my Monograph, which is in preparation, are completed.

A majority of the following forms belong, as will be observed, to Stigmatomyces, a distinctly dipterophilous genus, which must certainly prove very large and widely distributed. That it is at the same time very difficult from a systematic standpoint is evident from the material studied, and few single characters, even of the appendages, seem to be wholly reliable. In describing the species the two superposed cells above the foot are regarded as constituting the receptacle, the upper bearing the stalk-cell of the perithecium terminally, and that of the appendage laterally, in mature individuals; the appendage proper consisting of a more or less distinctly differentiated basal cell, which may or may not bear antheridia like the series of fertile cells superposed above it; the antheridia, though often single, are more often asymmetrically paired. The American species were obtained from small flies in part collected for me by Mr. W. T. Clarke at Berkeley, California, and in part by myself at Kittery Point, Maine, or in the vicinity of Cambridge during September, for the determination of which I am indebted to the kindness of Mr. D. W. Coquillett. The remainder, with the exception of the single African species on Diopsis, were all obtained from the Ralum collections of Professor Dahl already referred to.

Stigmatomyces rugosus nov. sp.

Venter of the perithecium dark amber brown, roughened by about ten transverse more or less irregular and sometimes anastomosing darker ridges formed by irregular wart-like elevations; evenly oval or elliptical, and abruptly distinguished from the rather stout neck, which is usually bent outward and about equal to it in length or somewhat shorter, distally distinctly enlarged, especially posteriorly; the tip beyond this enlargement abruptly somewhat narrower; the apex asymmetrical, the three posterior lip-cells forming three corresponding projections, rounded or bluntly pointed and more prominent than the bilobed papilla formed below them by the anterior lip-cells. Stalk-cell of the appendage small, subtriangular, amber brown, abruptly prominent below the relatively large dark brown basal cell, which, though narrower, nearly equals it in size, may or may not bear antheridia, and has a well-marked annular

thickening on the inner side of its wall at the base; the fertile cells above it, four or five in number, bearing the rather large antheridia in pairs; the series becoming obliquely lateral or external, the free necks strongly curved outward. The cells of the receptacle nearly equal, or the upper larger; the basal cell tapering to the foot and distally slightly broader than the subbasal cell. Spores about 40 × 4 μ. Perithecium: venter 72 × 45 μ; neck 62–72 × 15–18 μ. Appendage proper 60–70 μ, stalk-cell 18 μ. Receptacle 90–100 × 20 μ. Total length to tip of perithecium 250–290 μ.

On the legs, thorax, and abdomen of a minute fly. Berlin Museum, No. 1296. Ralum, New Pomerania.

A form from the same locality occurring on a small blackish fly, and also characterized by a roughened perithecium, differs in several points from that above described; but a description of this, as well as of a closely allied form from Kittery Point, Maine, is withheld for the present.

Stigmatomyces Diopsis nov. sp.

Colorless or slightly yellowish. Venter of the perithecium long-oval or elliptical, pale reddish amber, rather abruptly distinguished from the paler neck, which tapers but slightly, except at its base, is straight or slightly bent, and traversed by four broad longitudinal ridges which are corrugated by about six successive elevations and depressions; a seventh distal elevation, larger and more prominent than the rest, is present just below the tip, which is abruptly narrower and slightly curved; the apex asymmetrical, the posterior lip-cells forming a tripapillate prominence, the middle papilla larger and more prominent; the anterior lip-cells forming two small lateral papillae placed side by side in such a position that the apex appears to be laterally notched. Appendage erect or somewhat divergent, straight or slightly curved backward, the stalk-cell more than twice as long as broad, and more than half united to the subtriangular stalk-cell of the perithecium, distally constricted at its junction with the well differentiated squarish amber-brown sterile basal cell of the appendage proper; the eight or nine fertile cells above bearing for the most part two antheridia each, the series of antheridia external in the mature types. Spores about 40–45 × 5 μ. Perithecium: venter 80–87 × 50 μ; neck 72–82 × 18 μ. Appendage proper 70–75 μ, stalk-cell 25–30 μ. Receptacle 75 μ. Total length to tip of perithecium 270–290 μ.

On *Diopsis* sp., Berlin Museum, No. 860. Bismarkburg, Togo, West Africa. On the upper surface of the abdomen near the tip.

Stigmatomyces Scaptomyzae nov. sp.

Venter of the perithecium becoming reddish amber brown, nearly isodiametric, becoming distally enlarged; the nearly hyaline neck very abruptly distinguished, slender, straight, or curved, its lower third sometimes narrower; the tip hardly or not at all differentiated; the ápex asymmetrical, the anterior lip-cells forming two lateral papillate slightly divergent protrusions, the posterior lip-cells forming two similar protuberances above them, between which a slight projection may or may not be present. Stalk-cell of the appendage elongate, very abruptly broader than the very small deep brown squarish infertile basal cell; the fertile cells usually five in number, the antheridia with short curved divergent necks and produced in pairs, except the terminal one, which is conspicuously spiniferous, the whole series usually obliquely external. Receptacle hyaline, the basal cell mostly larger, longer, tapering below. Spores about 36 × 3.5 μ. Perithecium: venter 90–100 × 36–44 μ; neck 108 × 10–15 μ. Appendage 47–55 μ, the stalk-cell 25–30 μ. Receptacle 65–100 μ. Total length to tip of perithecium 300–325 μ.

On the abdomen and legs of *Scaptomyza graminum* Fallen. Kittery Point, Maine, vicinity of Cambridge, Mass., Berkeley, California.

Stigmatomyces Limnophorae nov. sp.

Venter of the perithecium relatively small, amber brown, the wall-cells becoming powdered by a darker maculation and separated by a corresponding number of well-defined unmodified longitudinal ridges which run somewhat obliquely and end, not abruptly, at the base of the neck: the latter generally slender, strongly bent throughout or even recurved, abruptly differentiated, sometimes of less diameter than the tip, which is distinguished from the rest of the neck by an abrupt enlargement more prominent anteriorly; the apex (in the not wholly mature types) unmodified, blunt, slightly oblique. Stalk-cell of the appendage rather prominently rounded externally, but not protruding abruptly below the basal cell, which nearly equals it in length and is slender, slightly larger distally, its base hyaline, its wall, which is dark amber brown above, becoming gradually thicker, so that the lumen of the cell is attenuated below, distally bearing two antheridia; the fertile cells above it, usually seven in number, forming a series outwardly recurved, the terminal cell apparently sterile, the two small cells below it bearing each a single antheridium, while the remainder bear two; the antheridia with short, broad, slightly recurved necks. Receptacle relatively large, hyaline, the basal cell ta-

pering slightly downward, the subbasal cell slightly longer and much broader distally. Perithecium: venter 55 × 30 μ; neck 75 × 10 μ. Appendage about 75–80 μ, stalk-cell 28 μ. Receptacle 110 × 25 μ. Total length to tip of perithecium 250–275 μ.

On the inferior surface of the abdomen and at the base of the posterior legs of a species of *Limnophorus*. Berkeley, California.

Stigmatomyces constrictus nov. sp.

Venter of the perithecium dark amber brown, subrectangular, or more or less inflated; the short stout neck about equal to it in length, very abruptly distinguished beyond the four rounded elevations which mark the distal ends of the brown wall-cells of the venter, subconical, with a considerable submedian enlargement often more prominent posteriorly; the tip often tapering to the five-papillate apex, the middle posterior papilla blunt and more prominent, the other four nearly symmetrical. Stalk-cell of the appendage often suboblong and externally prominent throughout its length; the basal cell narrower and longer, separated from it by a rather deep constriction and bearing one or two antheridia distally; while above it the two remaining fertile cells are very small, each bearing two antheridia; the series surmounted by a spiniferous antheridium, all the antheridia relatively large and almost free. Receptacle hyaline, its basal cell more or less elongate, tapering to a narrow base, a rectangular distal thicker walled portion separated by a thin incomplete septum; the subbasal cell much shorter, more or less abruptly and prominently inflated at its base, sometimes slightly also at its distal end, and having a more or less well defined median constriction, below which the inflated base may be separated by a thin partial septum. Perithecium: venter 54 × 30–40 μ; neck 44–55 × 18 μ. Appendage 43–50 μ, the stalk-cell 18 μ. Receptacle 70–90 × 22 μ. Total length to tip of perithecium 200–300 μ (those on the tips of the legs much smaller, 180–200 μ).

On the legs and abdomen of a small fly. Ralum, New Pomerania. Berlin Museum, No. 1294.

Stigmatomyces humilis nov. sp.

Venter of the perithecium amber brown, slightly inflated throughout and slightly asymmetrical; the neck rather abruptly distinguished, concolorous, but paler distally, generally shorter than the venter, stout, tapering to the blunt, hardly differentiated apex; about one third of its length taken up by the tip, which is distinguished from it by a slight broad constriction; the outer basal cells subequal and irregularly promi-

nent. Appendage relatively rather slender, very long, sometimes extending nearly to the middle of the neck of the perithecium, the stalk-cell separated by a slight constriction from the basal cell, which is relatively large, the annular thickening about the base on the inner side of its wall unusually well developed, amber brown, bearing two antheridia; the subbasal cell almost as large, bearing two antheridia, the two successive cells above it smaller and bearing each a single antheridium; the series completed by a single terminal antheridium; the antheridial necks rather slender, and tapering, somewhat appressed. Receptacle short, stout, the cells subequal. Spores about 28 × 3 μ. Perithecium: venter 46–55 × 32–37 μ; neck 45–47 μ. Appendage 65–75 μ, the stalk-cell 18 μ. Receptacle 55 μ. Total length to tip of perithecium 175 μ.

On the superior surface near the tip of the abdomen of a muscid somewhat larger than the other hosts from Ralum, New Pomerania. Berlin Museum, No. 1287.

Stigmatomyces dubius nov. sp.

Amber brown with the exception of the receptacle and the stalk-cell of the perithecium. Venter of the perithecium slightly inflated, relatively small, not abruptly differentiated from the broad neck, which gradually enlarges distally below the rather abruptly tapering, slightly bent tip; the middle of the three posterior projections from the lip-cells larger and longer than the others and bent over so as to overlap the anterior lip-cells, which are curved abruptly toward it; the two lateral posterior projections prominent beyond the base of the middle one, rather slender, and slightly curved inward. Stalk-cell of the appendage distally darker, abruptly prominent below the basal cell, which is small, squarish, and deeper brown; the rest of the appendage, which is unusually long, apparently proliferous above the spiniferous cell, extending beyond the venter of the perithecium, is made up of about eight cells, which bear rather long antheridia in pairs, their necks appressed usually in a lateral series. Receptacle relatively large, hyaline, the subbasal cell much longer and broader than the basal cell, which tapers but slightly to the small foot. Spores 30 × 3.5 μ. Perithecium: venter 58 × 40 μ; neck 110 × 25 μ. Appendage 80–95 μ, stalk-cell 25–32 μ. Receptacle 145–185 × 25–30 μ. Total length 350–375 μ.

On a fly with monstrously developed anterior legs resembling those of *Ochtheria mantis*. Ralum, New Pomerania. Berlin Museum, No. 1281 and 1298. On the head and at the base of the posterior legs.

Stigmatomyces gracilis nov. sp.

Form long and slender. Venter of the perithecium amber brown, relatively large above its narrow base, more or less inflated, often more distinct distally; the neck usually straight, sometimes curved, nearly hyaline as a rule, and abruptly distinguished; the tip abruptly but slightly narrower above a prominent and usually symmetrical inflation; the median posterior projection of the lip-cells erect, larger, and slightly more prominent than the two lateral ones, which diverge slightly and are nearly symmetrical with the two anterior ones. Stalk-cell of the appendage slightly prominent distally below the dark amber-brown basal cell, which may be more than half as large, bearing one or two antheridia; the remaining cells four in number, relatively large, except the fourth, which bears a large, curved, conspicuous spine below the base of the terminal antheridium; the antheridia in pairs, lateral or obliquely external, the necks short, becoming pointed and slightly divergent. Receptacle usually rather long and slender, straight or curved, hyaline; the two cells about equal, or the upper larger and distally often broader than the combined diameters of the cells above it. Spores $45 \times 3.5\,\mu$. Perithecium: venter $85–90 \times 30–40\,\mu$; neck $100–110 \times 16\,\mu$ (the enlargement $\times$ $20\,\mu$). Appendage $70–75\,\mu$, stalk-cell $18–25\,\mu$. Receptacle $90–125 \times$ $18–20\,\mu$. Total length to tip of perithecium $250–360\,\mu$.

On the same host with *S. dubius*. Ralum, New Pomerania. Berlin Museum, No. 1298. Near the tips of the posterior legs.

Stigmatomyces proboscideus nov. sp.

Venter of the perithecium amber brown, sometimes more than twice as long as broad, usually but slightly inflated, often more so distally; the neck lighter brown, rather abruptly distinguished, relatively very stout, elongate, nearly isodiametric, usually curved throughout; the short tip abruptly somewhat narrower, the apex broad and blunt without well developed elevations. Stalk-cell of the appendage brown, relatively small and short, slightly prominent distally; the basal cell broader than long, the five fertile cells above it rather short and stout, the series curved sidewise, the antheridia lateral in pairs. Spores about $30 \times 3\,\mu$. Perithecium: venter $75–95 \times 32–36\,\mu$; neck $135–185 \times 18–22\,\mu$. Appendage $55–72\,\mu$, stalk-cell $18\,\mu$. Receptacle $110–125 \times 29\,\mu$. Total length to tip of perithecium $400\,\mu$.

On the abdomen of a small fly. Ralum, New Pomerania. Berlin Museum, No. 1288.

Stigmatomyces Hydrelliae nov. sp.

Venter of the perithecium amber brown, oval, the wall-cells becoming separated by well-defined, slightly oblique longitudinal broad ridges, which become broader distally where they end abruptly; the neck pale, well distinguished, its middle third prominently inflated, more so posteriorly, and separated from the usually abruptly bent tip by a constriction; the apex rounded, one of the (lateral?) lip-cells forming a slender, bluntly pointed, well-defined free projection. Stalk-cell of the appendage sub-triangular, somewhat prominent below the basal cell, which nearly equals it in length, sterile; the fertile cells above it nearly equal, bearing rather large, apparently single, antheridia, with stout, straight necks, the series ending in a terminal spiniferous antheridium. Receptacle hyaline, the two cells nearly equal in length, the lower tapering below, the upper broader inflated, its diameter greater than the base of the perithecium and stalk-cell combined, so that the latter region appears to be constricted. Spores $28 \times 2\ \mu$. Perithecium: venter $50–55 \times 33–40\ \mu$; neck $40–43\ \mu$. Appendage $50\ \mu$, the stalk-cell $18\ \mu$. Receptacle $55–65 \times 20–22\ \mu$. Total length to tip of perithecium $150–185\ \mu$.

On the superior surface of the abdomen, sometimes on the legs of *Hydrellia* sp. Kittery Point, Maine. Occurring in scattered groups.

Stigmatomyces purpureus nov. sp.

Becoming wholly suffused with purple. Venter of the perithecium inflated toward the base, tapering distally; the four wall-cells separated by a corresponding number of prominent longitudinal ridges, rounded in section, which run spirally, making in well-developed individuals a whole half turn about the venter, and becoming sometimes lobulated through the presence of successive constrictions and enlargements; neck not abruptly distinguished, except by the abrupt elevations which form the terminations of the longitudinal ridges of the venter, rather slender, an abrupt posterior subterminal elevation preceded by a slight constriction, the tip distally quite hyaline; the apex becoming furcate through the presence of an anterior (shorter) and a posterior projection. Stalk-cell of the appendage relatively small, but slightly prominent below the basal cell, which is nearly as long, sterile, and, as a rule, followed by three cells bearing antheridia singly or in pairs, the terminal one spiniferous. Receptacle usually straight, the cells nearly equal or the upper larger. Spores $35 \times 3\ \mu$. Perithecium: venter $80–100 \times 45–50\ \mu$; neck $80–83\ \mu$. Appendage $55\ \mu$, the stalk-cell $18\ \mu$. Receptacle $100–120\ \mu$. Total length to tip of perithecium $200–325\ \mu$.

On all parts of *Scatella stagnalis* Fallen. Kittery Point, Maine, and vicinity of Cambridge, Mass., September. Fully developed individuals with the typical structure are uncommon, a majority of the numerous specimens examined having the color dull or paler purplish, the ridges less well defined, without lobulations and with less than a half twist; the neck and apex hardly, if at all, modified. The same host is infested by an amber-brown form which may prove a mere variety of that above described, being scarcely distinguishable structurally from the less well-marked individuals of this species, the type form of which is, from its remarkable color and the structure of its perithecium, one of the most peculiar members of the genus.

Stigmatomyces spiralis nov. sp.

Venter of the perithecium relatively long and slender, flask shaped, or more often but slightly if at all inflated, the granular wall-cells distinguished by a corresponding number of abrupt, narrow, longitudinal prominent ridges, which become minutely roughened, and are spirally twisted so as to describe a full half turn; the neck concolorous, distinguished by the abruptly elevated and abruptly broadened terminations of the longitudinal ridges of the venter, as long as or slightly shorter than the venter, slightly curved or sometimes straight, nearly cylindrical or slightly tapering; the tip slightly but abruptly narrower, relatively short, somewhat asymmetrical; the apex nearly symmetrical, four papillae being arranged about a somewhat more prominent central projection. Appendage rather short and stout, distinctly broadened in the middle, the stalk-cell stout, the basal cell half as large, or less, and fertile; the series of six to eight fertile cells above it surmounted by a single antheridium, and distinguished by slight successive constrictions, broad and much flattened, each bearing a single antheridium, the fifth furnished with a very sharp spine; the antheridia forming a usually lateral series, their necks becoming strongly curved. Receptacle elongate, slender, becoming brownish or yellowish, the upper cell often more than twice as long as the basal. Spores $22 \times 2.5\,\mu$. Perithecium: venter $90–165 \times 35–47\,\mu$; neck $90–160 \times 17\,\mu$ (the tip $25–30\,\mu$). Appendage $40–50\,\mu$, the stalk-cell $15\,\mu$. Receptacle $100–250 \times 15\,\mu$. Total length to tip of perithecium $350–600\,\mu$ (average $500–550\,\mu$).

On *Hydrina* sp., Kittery Point, Maine. Usually on the upper surface of the thorax, less often on the legs and elsewhere.

Stigmatomyces Limosinae nov. sp.

Perithecium amber brown, the venter slightly inflated, the neck not abruptly distinguished, tapering slightly; the tip usually abruptly narrower, the posterior lip-cells forming an inconspicuous irregular truncate or rounded bilobed projection somewhat more prominent than a similar projection formed by the anterior lip-cells; basal cells relatively very large, forming a short, well-defined stalk, hyaline or colored above, often carrying the base of the perithecium beyond the tip of the appendage, and consisting of an inner cell next the appendage and two superposed outer ones, the lower of which (secondary stalk-cell) is smaller; the stalk-cell below these wholly united to the stalk-cell of the appendage, rather stout and short, separated from the cells above it by a horizontal septum, which may be slightly oblique or (as in the California variety) strongly oblique, in which case the secondary stalk-cell extends downward beside the stalk-cell so that only the lower third or quarter of the latter is free externally. Stalk-cell of the appendage relatively large, as long as or often longer than that of the perithecium and about half as broad, usually bulging externally, its outer margin usually curved symmetrically from its base to the base of the basal cell; the latter relatively small, deep amber brown, half as long as broad, pointed distally between the antheridium which arises from its inner side and the base of the first fertile cell above it, which, with the other fertile cells, are large and prominent, thick walled, much flattened, and obliquely superposed, distinguished by rather deep constrictions, seven to ten in all, or rarely more (seven to fourteen in the Californian form), the original number being increased by the terminal proliferation of the appendage; the antheridia borne on the inner side of the appendage, their very long but not abruptly differentiated necks extending obliquely upward, appressed in a double series; the upper antheridia often infertile, becoming septate and irregularly swollen. Receptacle relatively short, the two cells nearly equal. Spores $28 \times 3\,\mu$. Perithecium: venter $50–90 \times 40–54\,\mu$; neck $90–125 \times 15–18\,\mu$; stalk (basal cells only) $72–100 \times 25–35\,\mu$. Appendage $60–100\,\mu$, stalk-cell $30–45\,\mu$. Receptacle $70–75 \times 22\,\mu$. Total length to tip of perithecium $250–360\,\mu$. Specimens on legs often much smaller.

On *Limosina fontinalis* Fallen. Kittery Point, Maine, vicinity of Cambridge, Mass., Berkeley, California. Usually in a dense tuft on the side or near the tip (inferior) of the abdomen and near the base of the posterior pair of legs. The Californian material, from two specimens of the host, differs constantly from the abundant New England material as

noted in the description, as well as from the fact that the venter of the perithecium is longer and less distinctly inflated, while its apex shows no perceptible modification of the lip-cells.

Stigmatomyces Papuanus nov. sp.

Venter of the perithecium dark amber brown, relatively small and rather prominently inflated, oval to elliptical; usually not abruptly distinguished distally from the hyaline or yellowish neck, which in well-developed specimens is very elongate, tapering very gradually, in others shorter and stouter; the tip clearly distinguished (abruptly so in the shorter forms), subconical, the posterior lip-cells forming a narrow, subtruncate, slightly recurved apical projection beyond the two laterally placed, papillate, slightly divergent projections of the anterior lip-cells; the basal cells forming a short, stout stalk, separated from the stalk-cell by an oblique septum. Appendage relatively small, resembling that of the *S. Limosinae* in general form, the fertile cells not more than five or six in number, the upper ones separated by constrictions which may be obsolete between the lower ones. Receptacle relatively short, the cells subequal, yellowish. Spores about $20 \times 2\ \mu$. Perithecium: venter $50–55 \times 40\ \mu$; the neck $90–290 \times 20\ \mu$; the stalk $35–45 \times 33–36\ \mu$. Appendage, $35–45\ \mu$, the stalk-cell $22–30 \times 14–17\ \mu$. Receptacle $55–72\ \mu$. Total length to tip of perithecium $400–485\ \mu$. A few specimens on the legs much smaller.

On three small flies of different species allied to *Limosina*. Ralum, New Pomerania. Perhaps a variety of *S. Limosinae*.

Arthrorhynchus Cyclopodiae nov. sp.

Becoming tinged with brownish yellow except the hyaline stalk-cell of the perithecium. Perithecium nearly straight and symmetrical, slightly inflated, usually distinctly constricted in the region of its very small basal cells just above the very large hyaline stalk-cell, which may nearly equal it in length and diameter and is often somewhat enlarged distally: the venter comprising the lower two-thirds, not clearly distinguishable from the neck, which tapers slightly and almost symmetrically, the tip fairly well distinguished above a more or less distinct enlargement, from which it is separated by a slight constriction; the apex consisting of a crown of four nearly symmetrical, distinctly tridentate, erect, or very slightly divergent projections, which are subtended by a corresponding number of slight elevations, the middle lobe of each projection more prominent than

the lateral and like them bluntly rounded. Receptacle consisting of two small cells, the lower twice as large as the upper, which gives rise distally to the stalk-cell and bears the free appendage laterally; the foot an unmodified cell which penetrates the host, dividing below into a very copiously branched system of slender, sinuous, rhizoidal hyphae. Appendage consisting of a dumbbell-shaped, free stalk-cell, the basal half-rounded or flattened, brownish, somewhat larger than the distal portion, which is deeper brown, flattened and inflated, connected by a narrow hyaline isthmus (the lumen of which may become almost obliterated) with the lower half, and mostly broader than the base of the basal cell of the appendage, which is infertile, subrectangular, or somewhat inflated, slightly longer than broad, the lower half of the walls becoming conspicuously modified by a progressive thickening from above downward, the thickened portion deeper brown; the remaining cells of the appendage three to four in number, brownish, successively smaller from below upward, giving the organ a characteristically tapering habit; the two lowest of these cells usually relatively shorter, and bearing each three to four antheridia side by side, distally and externally; those above relatively longer and narrower and producing fewer antheridia, the terminal one spiniferous. Antheridia with slender curved necks. Spores 60–65 × 4.5 μ. Perithecium: venter 325–350 × 70–90 μ; the stalk-cell 220–250 × 75–80 μ. Appendage, 100–110 μ, the stalk-cell 35–40 × 30–35 μ (the upper half × 28–30 μ). Receptacle 55–75 × 45–50 μ.

On the abdomen of *Cyclopodia macrura* Speiser. New Pomerania. Berlin Museum, No. 854.

The original name given to this genus in 1857 by Kolenati is here retained in preference to the much later one applied to it by Peyritsch in 1873; since however absurd and scientifically worthless the original zoölogical descriptions of these forms may be, there has never been the slightest question as to the generic identity of the organisms studied by these two authors. Neither the descriptions nor the figures given by Kolenati and Diesing are, however, sufficient to render a specific determination possible, so that the name given by Peyritsch to the European species of the genus, although it is undoubtedly a synonym of *A. Diesingii* Kol. or *A. Westrumbii* Kol., or more probably of both, may properly be retained. The new forms here described are very closely allied, differing chiefly in the details of structure in the appendage and the tip of the perithecium, but are very different from *Arthrorhynchus Nycteribeae.* Material in my possession obtained from species of *Nycteribia*, from Europe, must, I think, be referred without question to the

last named species; although the conformation of the tip of the perithecium has apparently been incorrectly reproduced in Peyritsch's plate.

Arthrorhynchus Eucampsipodae nov. sp.

Hyaline throughout. Perithecium straight or distally slightly curved, tapering gradually from the middle, or lower, to the broad tip; the apex consisting of a slight median projection surrounded by a crown consisting of four slightly shorter, broad, blunt, distinctly divergent projections, which show indistinct marks of lobing and are symmetrically placed; the stalk-cell about one half as long as the perithecium or less. The basal cell of the appendage constricted in the middle as in the preceding species, the lower half irregularly rounded and four or five times as large as the upper half, which is very small, colorless, and less than half as wide as the cell above it; the fertile cells three in number, the lower bearing four or (?) five antheridia, the upper three in addition to the terminal one, which is furnished with a short hyaline basal spine; the necks of the antheridia large, tapering, divergent. Receptacle as in the preceding species. Spores about 45–50 × 4 μ. Perithecium: venter 250–325 × 65–75 μ; the stalk-cell 110–150 × 55 μ. Appendage, 75–90 μ, the stalk-cell 35 × 25 (the upper half × 10 μ).

On the abdomen of *Eucampsipoda Hyrtli* Kol., Egypt. Berlin Museum, No. 855.

Rhizomyces gibbosus nov. sp.

General habit more or less sigmoid. Perithecium amber brown, concolorous, with its relatively large basal cells, from which it is hardly distinguished, asymmetrically inflated, bent, and tapering somewhat distally; a subterminal abruptly rounded enlargement, beyond which the short asymmetrical tip is clearly distinguished, bearing a large two-celled outgrowth posteriorly, the lip-cells being otherwise unmodified: stalk-cell hyaline, variably, sometimes greatly elongated, separated from the basal cells by a more or less distinct constriction. Appendage nearly hyaline, except the small deep brown sterile basal cell, the remaining cells, three to seven in number, bearing short one- to two-celled branches distally and laterally on which the free flask-shaped antheridia are borne singly or several together. Receptacle short and stout, the upper cell several times as large as the basal cell, which appears to penetrate the host directly by means of a rhizoidal apparatus. Spores about 35 × 3 μ. Perithecium, including basal cells, 85–108 × 30–36 μ; the stalk 60–160 × 18–20 μ. Appendage 65–110 μ. Total length to tip of perithecium 180–325 μ.

On the upper surface near the tip of the abdomen of a species of *Diopsis*. Berlin Museum, No. 850. Tanga, Africa.

CERAIOMYCES nov. gen.

Structure of perithecium as in Laboulbenia, its stalk-cell united to the free base of the free stalk-cell of the appendage, which bears a well differentiated basal cell terminally, from the end of which are borne antheridial branches, the successive cells of which produce terminally either successive secondary branchlets or antheridia or both, much as in Laboulbenia. Receptacle two-celled.

Ceraiomyces Dahlii nov. sp.

Perithecium large, blackish brown, with an olive shade, becoming opaque, usually slightly curved, tapering gradually to the slender undifferentiated tip; the anterior lip-cells forming two appressed hyaline-tipped finger-like projections; the base very broad, translucent, dull brownish, bulging conspicuously below the venter, especially on the left side; the stalk-cell small, nearly isodiametric, united on its inner side to the base of the stalk-cell of the appendage. The latter free, though often in contact with the base of the perithecium, dull blackish olive, outwardly inflated, narrower terminally where it bears the characteristically differentiated basal cell of the appendage, which becomes almost opaque and is somewhat flask- or bottle-shaped with a rounded extremity, from which, typically, two divergent branches arise which in turn may branch one to three times sub-dichotomously; the long slender flask-shaped antheridia borne, one to two together, distally from the successive cells. The basal cell of the receptacle nearly spherical, penetrating the host by a long filament which is slender except for an enlargement immediately below the integument of the host, simple at first but becoming more or less copiously branched; the upper cell very large and elongate. Spores about $30 \times 3\,\mu$. Perithecium $275–310 \times 55–60\,\mu$; the base, including the stalk-cell, $68–72 \times 58–68\,\mu$. Appendage $75–85\,\mu$ (the basal cell $18 \times 12\,\mu$), the stalk-cell $40–45 \times 18–22\,\mu$. Receptacle $175–240 \times 35\,\mu$ (the basal cell $20–22\,\mu$). Total length to tip of perithecium $400–675\,\mu$, average $550\,\mu$.

On various parts of a small flower fly. Ralum, New Pomerania. Berlin Museum, Nos. 1283 and 1298. Occurring more often on the head, where it might be mistaken for a dipterous antenna.

Dimeromyces coarctatus nov. sp.

Male Individual. Receptacle nearly hyaline, consisting of usually three superposed cells, the upper separated by a dark-colored constriction

from a short, simple, two- to three-celled hyaline or brownish appendage. The antheridia usually two, seldom three, borne singly from the successive cells of the receptacle, from which they are separated by a small basal cell; the venter having an external depression and not abruptly distinguished from the stout curved neck. Receptacle 35–45 × 6–7 μ. Appendage 25–50 μ. Antheridia 18 × 5 μ.

Female Individual. Receptacle consisting of a large basal cell about twice as long as broad, bulging so as to form a rounded base which pushes the small brownish-black foot to a lateral or sublateral position; the remaining cells, usually eight or nine in number, separated by horizontal septa and superposed in a simple series; the lower cells greatly flattened, those above somewhat less so, the series ending in a somewhat abruptly narrower terminal cell, which is more than twice as long as broad, subcylindrical, its extremity rounded symmetrically and bearing a short, simple, usually four-celled terminal brownish appendage, which is distinguished by a constricted dark basal septum and terminated by a somewhat inflated lighter larger cell, which becomes characteristically disorganized on one side, so that the appendage appears to end in a slender curved projection. The remaining cells of the receptacle producing single appendages or perithecia, except the basal and sometimes a subbasal cell. The uppermost of these secondary appendages arises from the inner side of the subconical subterminal cell of the receptacle, occupying a position in the median line between the primary appendage and the base of the first perithecium, and consists of a short subconical basal cell, from the narrow extremity of which the simple, several-celled terminal portion is distinguished by a constricted dark septum; the remaining appendages laterally divergent on opposite sides in such a way as to appear paired, usually three on each side, each consisting of a rather long basal cell inflated along its upper side so as to appear more or less geniculate, concolorous with the receptacle, its narrower extremity suffused with dark brown, distinguished without constriction by a dark septum from the simple terminal portion, which is usually five-celled, more or less strongly recurved, brown, its terminal cell becoming inflated and undergoing gelatinous degeneration on the lower side, which causes it to appear split in two, the hook-like upper half of the cell alone persisting in some individuals. Perithecia yellowish, distally brownish, one, rarely two, in number; the first always arising from the cell immediately below that which bears the upper secondary appendage, the second, when one is present, replacing one of the appendages lower down; consisting of a symmetrically inflated venter, which tapers gradually downward, passing into the short stalk; a short neck

rather abruptly distinguished, deeper brown below, its tip inflated below four terminal projections, three or two of which are in the form of rounded papillae of unequal size, and one or two of which are pointed and much more prominent. Spores 42 × 3.5 μ. Perithecium, including the stalk, which is continuous with it, 125 × 20–35 μ. Receptacle to base of primary appendage 50–75 μ. Secondary appendages about 75 μ. Total length to tip of perithecium 150–180 μ.

Densely crowded on the inferior surface of the abdomen or rarely on the legs of a small pale fly, remarkable for a prominent black spur-like bristle on the posterior legs. Ralum, New Pomerania. Berlin Museum, No. 1282.

Dimeromyces rhizophorus nov. sp.

Male Individual. Receptacle consisting of a basal cell which penetrates the host directly without a differentiated foot, and two to three superposed cells above it, each of which usually bears an antheridium, the upper terminated by a short, pointed, slender cell. The antheridia rather short and stout, with short, stout necks. Receptacle about 50 × 8 μ. Appendage 12 × 3.5 μ. Antheridia 25 × 9 μ.

Female Individual. More or less deeply tinged with amber brown. Receptacle amber brown, consisting of six superposed cells, the small basal cell, hardly visible above the integument, penetrates the host directly by means of a very large, abruptly furcate rhizoid, the two cells above it similar, broader than long, bearing each an appendage consisting of a basal cell bent toward the receptacle, darker and narrower distally, and separated by a dark septum from the three-celled terminal portion, which is straight or slightly curved, larger toward the middle, the smaller terminal cell becoming partly disorganized. The next (fourth) cell of the receptacle bears the single perithecium; the distal terminal cell longer and narrower, and terminated by a short, pointed, one- sometimes two-celled primary appendage (similar to that of the male individual), from which it is separated by a constriction; the subterminal cell narrower distally, producing on its inner side an appendage similar to those below it, but straight and somewhat shorter. Perithecium with a short stout stalk rapidly expanding into the asymmetrically inflated deeper brown venter of the perithecium; the neck very short and abruptly distinguished; the tip relatively large, four-lobed, inflated with two lateral papillate outgrowths, above which the lips form a subconical projection.

Spores about 25 × 3 μ. Perithecium including stalk 70–90 × 20–

25 μ. Receptacle about 45 × 12 μ. Primary appendage 12 μ; secondary appendages 35–40 μ. Penetrating rhizoidal branches 150–184 × 10–12 μ. Total length to tip of perithecium 90–110 μ.

On the inferior surface of the abdomen of a small fly. Ralum, New Pomerania. Berlin Museum, No. 1295.

Dimeromyces crispatus nov. sp.

Male Individual. Receptacle consisting of four superposed hyaline cells, the basal one much longer than the rest combined; the upper bearing distally a two-celled terminal appendage, the lower cell of which is small, the upper elongate, brownish; the two remaining cells of the receptacle producing each a single antheridium. Antheridia superposed, the stalk-cell, neck, and venter well distinguished, the latter symmetrically and considerably inflated, the neck slightly curved. Receptacle 50 × 8 μ. Antheridia 33 × 8–9 μ. Appendage 36 μ.

Female Individual. Receptacle consisting of usually five superposed cells, the basal cell very elongate, slender, and hyaline; while of the four remaining cells the two lower are much flattened, broader than long, and separated by oblique septa, the two upper unlike and narrower. Of these four cells the second from below gives rise to the stalk-cell of the perithecium, while the others by successive proliferation produce each a branch consisting of eight or ten obliquely superposed cells; while each of these cells in turn produces a single simple branchlet from its upper side, originally terminal, but becoming lateral through the further proliferation of the cell which bears it; the branchlets distinguished by a slight constriction and a broad dark septum at the base, brown, curved, distally helicoid, slightly enlarged and paler. The primary terminal appendage thus appears as the lowest of the upper series of branchlets, from which it does not differ in structure. Perithecia one to three in number, the first lowest, and always formed from the second from below of the four distal cells of the receptacle, others sometimes arising from each of the two upper distal cells; the stalk hyaline, long and slender, the venter small, narrow, not distinguished from the stalk, becoming brownish, distally slightly inflated, the neck short and well but not abruptly distinguished; the tip well differentiated, hyaline, symmetrical or nearly so, shovel shaped or spatulate, swollen at its base, and tapering to the broad, bluntly rounded or nearly truncate apex. Spores about 30 × 3.5 μ. Perithecium: 70–75 × 18 μ. the stalk 50–125 × 15 μ. Receptacle, basal cell 185–250 × 18 μ, the distal portion about 50 μ. Total

length to tip of perithecium 360–435 μ. Lateral cell series or branches about 50 μ long, their branchlets to tip of helix about 50 μ.

On the legs and superior surface of the abdomen of the same host parasitized by *D. coarctatus*. Ralum, New Pomerania. Berlin Museum, No. 1282.

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CONTRIBUTIONS FROM THE ZOÖLOGICAL LABORATORY OF THE MUSEUM OF COMPARATIVE ZOÖLOGY AT HARVARD COLLEGE. E. L. MARK, DIRECTOR. — No. 119.

A STUDY OF VARIATION IN THE FIDDLER CRAB GELASIMUS PUGILATOR Latr.

By Robert M. Yerkes.

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BY ROBERT M. YERKES.

Presented by E. L. Mark, February 13, 1901. Received March 4, 1901.

CONTENTS.

I. INTRODUCTION.

THIS study was undertaken to get light on some minor problems of variation, and to furnish records for future reference.

The matter of future reference seems to me of special importance, for it is evident that with records of the variations of a race during stated intervals available, the course and progress of evolution may be more or less accurately traced. Davenport ('99) has emphasized the need of the collection and filing of statistics of variation, especially of *Place-Modes;* and it was in response to his plea for this kind of work that I undertook to determine some place-modes for one of the Fiddler Crabs (Gelasimus pugilator) of a certain region.

In order to make the records of measurements together with my computations and interpretations available for any who may, in the future,

desire to use them, they will be placed in the Library of Harvard University, subject to the order of either the librarian or the writer.

Through the kindness of Mr. Alexander Agassiz and the authorities of the United States Fish Commission Station at Wood's Hole, Massachusetts, I was permitted to occupy, during a part of the summer of 1899, one of the tables in the Fish Commission Laboratory controlled by the Museum of Comparative Zoölogy. I desire to thank them for the privilege, and also Professor H. C. Bumpus, Director of the Laboratory, for facilities in collecting material and for many courtesies which made work pleasant. To Professor E. L. Mark I am indebted for suggestions and assistance in the arrangement of this report; to Professor C. B. Davenport I owe the knowledge and interest which led me to the problems, and to him I am also indebted for invaluable assistance in the prosecution of the work.

II. Problems.

The original purpose of this work was the determination of place-modes for Gelasimus pugilator of West Falmouth, Mass. Examination of the material for measurement and consideration of the probable value and significance of various dimensions led to the inclusion of several other problems. For it seemed advisable to select for the determination of place-modes such measurements as would be likely to contribute data for problems of adult form, of development, and of function.

The male Fiddlers are either right- or left-handed, one chela being enormously developed, the other small. The proportions of right- and left-handed animals will be considered later. In the females the chelae are nearly equal. One immediately asks: (1) What is the meaning of this condition in the males? (2) What relation does the size of the chela bear to the other body measurements? (3) What determines whether an animal shall be right- or left-handed? These are some of the problems which, it was hoped, might be at least partially solved by a quantitative study of variation; for unquestionably this method can supplement in important ways histological and physiological studies.

It was my purpose to measure equal numbers of the two species of Fiddlers, Gelasimus pugilator and G. pugnax, found in the vicinity of Wood's Hole,* selecting equal numbers of males and females from each of the two species. But the task of measuring was slow, and the time then available for the work was exhausted before its completion. This

* G. minax does not occur in the vicinity.

report, therefore, represents only a fragment of what was planned, and what the complete solution of the suggested problems demands.

III. Methods and Material.

The following measurements were made: —

1. Frontal Breadth, the distance between the anterior marginal points of the carapace (Figure 1, *FB*).

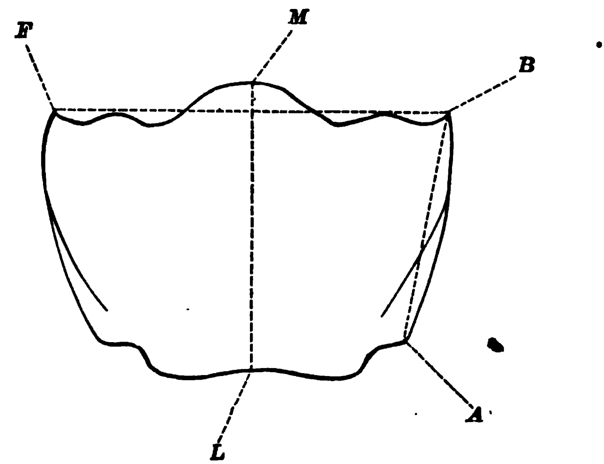


Figure 1. Dorsal aspect of carapace. *BA*, right marginal length. *FB*, frontal breadth. *ML*, median length.

2. Median Length, the maximum length of the carapace in the median plane. (Figure 1, *ML*).
3. Right Marginal Length, the distance from the right anterior marginal point of the carapace to the posterior end of the lateral ridge, just above and between the fourth and fifth legs (Figure 1, *BA*).
4. Left Marginal Length.
5. Meropodite of the Right Chela, the distance between the articulations on the anterior face. The proximal point of measurement, *i. e.* the articulation between ischiopodite and meropodite, is on the anterior ventral surface, and therefore does not show in Figure 2.
6. Carpopodite of the Right Chela, the distance between the anterior articulations (Figure 2, *CL*).
7. Propodite of the Right Chela, the distance from anterior articulation with carpopodite to articulation with dactylopodite (Figure 2, *PL*).

8. Meropodite of Left Chela.
9. Carpopodite of Left Chela.
10. Propodite of Left Chela.
11. Meropodite of Second Right Leg; points the same as for meropodite of chela.
12. Meropodite of Second Left Leg.

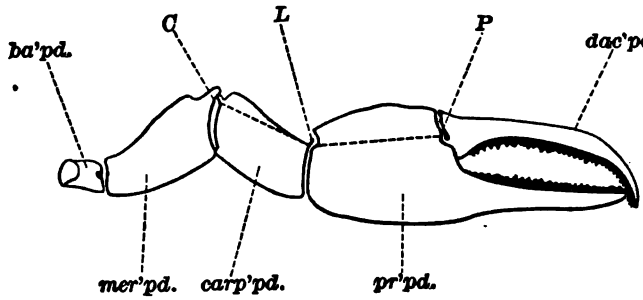


FIGURE 2. Dorsal surface of Right Chela. *dac'pd.*, dactylopodite; *pr'pd.*, propodite; *carp'pd.*, carpopodite; *mer'pd.*, meropodite; *ba'pd.*, basipodite; *CL*, length of carpopodite; *LP*, length of propodite.

The above measurements are similar to those made for Carcinus maenas by Weldon ('93), but in no case identical with his. He has, furthermore, expressed all measurements in terms of total carapace length, so comparison of our results is impossible. Dr. H. W. Rand * has repeated Weldon's measurements on C. maenas at Wood's Hole. His results, which have not as yet been published, will furnish, in connection with this study, interesting data for the comparison of Carcinus and Gelasimus.

The measuring apparatus used consisted of a pair of spring dividers, which could be adjusted easily and accurately by means of a thumb-screw. In measuring, the end of one arm of the dividers was fixed upon the point marking one limit of the dimension to be measured and the other arm was adjusted by means of the thumb-screw until its point coincided with the other limit of the dimension. The dividers were then transferred to a steel millimeter scale, above which a pocket lens was so arranged as to give a magnification of about twelve diameters, thus enabling one readily to read from the scale the distance between the points of the dividers. The scale was ruled to fifths of a millimeter, and by determining whether the fine point of the arm rested in or between

* Data and description of measurements, in manuscript.

marks it was possible to read to tenths. Although in case of these measurements readings were made to tenths, accuracy to fifths is all that can be claimed, because of the tendency to judge in favor of the marks on the scale.

Over a thousand individuals of Gelasimus pugilator were collected, without any attempt at selection, from a large colony on the shore of West Falmouth Harbor, between July 24th and August 22d. The accompanying map of the harbor and vicinity shows the location of the colony; two small circles mark the limits of the ground used for collecting.

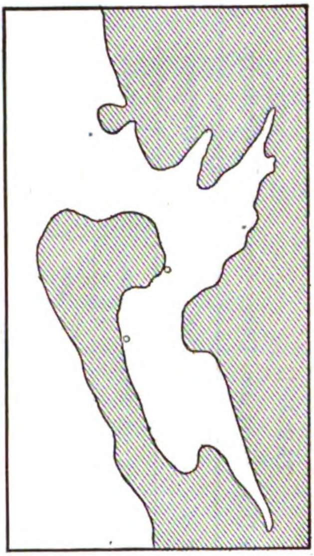


FIGURE 3. Map of West Falmouth Harbor. Material was collected from the region between the small circles.

Weak alcohol, about 20%, gave satisfactory results as a killing agent. Substances which act very quickly, such as hot water, formol, or strong alcohol, cause autotomy.

Twelve measurements were made for each of four hundred right-handed animals, and for the same number of left-handed individuals. For these two groups of measurements the means, modes, standard deviations, and coefficients of variability have been found.

To avoid the possibility of misunderstanding as to the meanings of these terms, I shall briefly define them.* The Mean is the sum of the products of each class into the number of individuals in the class, divided by the total number of individuals. The Mode is the class containing the greatest number of individuals. The Standard Deviation "is found by adding the products of the squared deviation-from-the-mean of each class multiplied by its frequency, dividing by the total number of variates, and extracting the square root of the quotient."† The Coefficient of Variability is one hundred times the quotient of the standard deviation divided by the mean.

* The terms and methods given by Davenport ('99[a]).

† Davenport ('99[a], p. 15).

TABLE I.

MEANS, MODES, STANDARD DEVIATIONS, AND COEFFICIENTS OF VARIABILITY.

Gelasimus pugilator (Males.)	Mean.		Mode.		Standard Deviation.		Coefficient of Variability.	
	Rights.	Lefts.	Rights.	Lefts.	Rights.	Lefts.	Rights.	Lefts.
	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.
Frontal breadth	15.728	15.658	15.55	15.15	1.1043	1.1699	7.022	7.471
Median length	12.245	12.237	11.95	11.95	.8898	.9298	7.266	7.598
Right lateral margin	8.842	8.285	8.35	7.95	.7821	.7460	8.845	9.000
Left lateral margin	8.400	8.716	8.35	8.35	.7265	.7743	8.649	8.880
Meropodite of right chela	8.780	5.812	8.75	5.15	.7900	.5270	9.000	9.920
Carpopodite of right chela	7.115	2.969	7.15	2.95	.7283	.3307	10.166	11.139
Propodite of right chela	9.248	2.733	9.35	2.75	.9457	.2438	10.215	8.898
Meropodite of left chela	5.563	8.656	5.55	8.35	.4859	.8359	8.734	9.657
Carpopodite of left chela	3.050	6.878	2.95	6.75	.2903	.7048	9.518	10.472
Propodite of left chela	2.710	9.038	2.75	9.15	.2253	.9270	8.318	10.255
Meropodite of 2d leg, right	7.589	6.965	7.15	6.75	.6484	.6379	8.479	9.160
Meropodite of 2d leg, left	7.127	7.523	6.75	7.15	.6218	.7273	8.724	9.660

IV. Results.

1. *Tables of Means, Modes, Standard Deviations, and Coefficients of Variability.*

Table I. contains the results of all calculations so arranged as to facilitate comparison of right- and left-handed animals. The first of each pair of columns gives the values for the right-handed individuals, — indicated at the top by "Rights;" the second, for the left-handed, — indicated by "Lefts."

It is to be noted that no identical measurements for Rights and Lefts (for sake of brevity we shall hereafter speak of the two types as Rights and Lefts instead of right-handed and left-handed) are strictly comparable, except frontal breadth and median length, for in every other case there is marked asymmetry, and the *measurements for the left side of one type have to be compared with those for the right side of the other.*

TABLE II.

Means and Coefficients of Variability arranged for Direct Comparison.

Gelasimus pugilator (Males).	Mean.		Coefficient of Variability.	
	Rights.	Lefts.	Rights.	Lefts.
	mm.	mm.	mm.	mm.
Frontal breadth	15.728	15.658	7.022	7.471
Median length	12.245	12.237	7.266	7.598
Lateral margin, great chelar side . .	8.842	8.716	8.845	8.880
Lateral margin, small chelar side . .	8.400	8.285	8.649	9.000
Meropodite of great chela	8.780	8.656	9.000	9.657
Carpopodite of great chela	7.115	6.878	10.166	10.472
Propodite of great chela	9.248	9.088	10.215	10.255
Meropodite of small chela	5.563	5.812	8.784	9.920
Carpopodite of small chela	3.050	2.969	9.518	11.139
Propodite of small chela	2.710	2.733	8.318	8.898
Meropodite of 2d leg, great chelar side	7.589	7.523	8.479	9.600
Meropodite of 2d leg, small chelar side	7.127	6.965	8.724	9.160

Table II. gives the means and coefficients of variability which are directly comparable. In every case, with the exception of the propodite of the small chela, the means for the Rights are larger than those for the Lefts; the coefficients of variability are without exception greater for the Lefts. In other words, the right-handed individuals are the larger and the less variable.

TABLE III.

Right- and Left-Handedness.

	G. pugilator.			G. pugnax.
	Males.		Females.	
	Rights.	Lefts.		
Lot from W. Falmouth, Aug. 18, 1899.	215	185	90	85
Lot from W. Falmouth, Aug. 22, 1809.	286	280	151	110
Totals.	501	465	241	195
Per cent.	51.86 of males.	48.14 of males.	20.00 of all	

TABLE IV.

Right- and Left-Handedness.

	G. pugilator.			G. pugnax.		
	Males.		Females.	Males.		Females.
	Rights.	Lefts.		Rights.	Lefts.	
Lot from W. Falmouth, July 16, 1900.	431	431	195	552	578	54
Per cent.	50 of males.	50 of males.	18.45 of all.	48.85 of males.	51.15 of males.	4.56 of all.

2. *Tables of Occurrence of Right- and Left-Handedness.*

In this connection a statement of the relative frequencies of right- and left-handedness is important. Table III. offers an analysis of two lots of pugilator and pugnax from West Falmouth. Of 966 males 51.86% were right-handed, 48.14% left-handed. During the summer of 1900 additional evidence was obtained on this subject. Over two thousand Fiddlers from the same colony were examined, with the results shown in Table IV. Comparison of these two tables (III. and IV.) indicates that the male Fiddlers are about equally divided into right- and left-handed individuals. The number of females captured was always small, probably because the males remain outside to fight, while the females and immature individuals scurry into the burrows. According to Table IV. the percentage of female pugilators captured was four times as large as that of female pugnax, but for this I am unable at present to offer any explanation.

3. *Polygons of Frequency.*

We shall now consider the various measurements individually, and examine the *Polygons* (more accurately Rectangles) *of Frequency.*

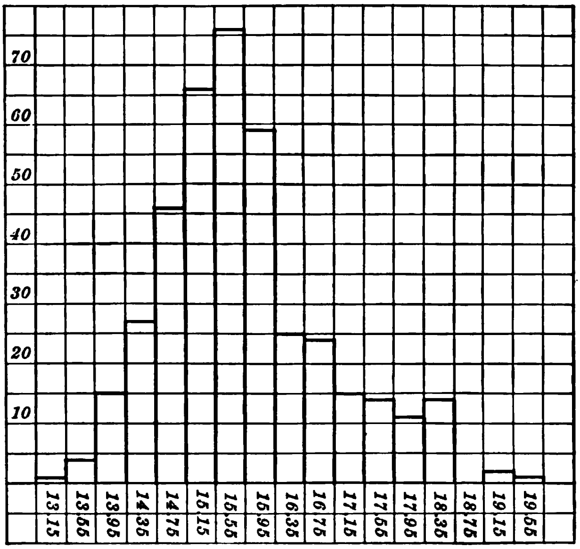
The polygons are all constructed thus. Each vertical column represents a class, and each of the squares in these columns represents five individuals. The classes are separated by 0.4 mm.* In polygon No. 1R, for example, the first class is 13.15 mm. and contains one individual; the second class is 13.55 mm. and contains four individuals.

1. *Frontal breadth.* This is the largest and least variable dimension of the twelve under consideration. Polygon No. 1R represents the distribution, among the various classes, of the right-handed individuals, and No. 1L that of the left-handed. Comparison of these two polygons shows a larger number of individuals in the modal class of the Rights than in that of the Lefts, indicating less variability among the right-handed animals. The curves† are both unsymmetrical. This lack of symmetry is probably due, as polygon No. 1L especially indicates, to the fact that the curves are really compound. In No. 1R the modes of the component curves are 15.55 and about 17.55; in No. 1L, 15.55 and about 17.15. In both cases the modal class 15.55 contains many more individuals than the mode at 17.15 or 17.55. Professor Davenport has

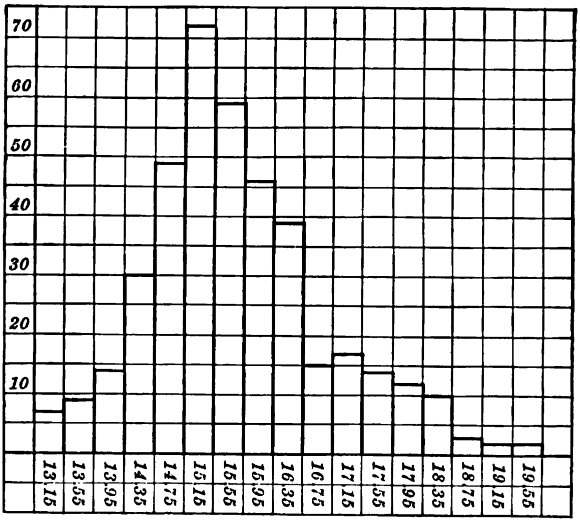
* Except in case of the carpopodite and propodite of the small chela, where they are separated by 0.2 mm.

† That is, the curve given by a line passing through the tops of the central ordinates of the rectangles.

suggested that these compound curves probably represent two successive stages separated by an ecdysis, and inasmuch as the animals measured



POLYGON No. 1R.

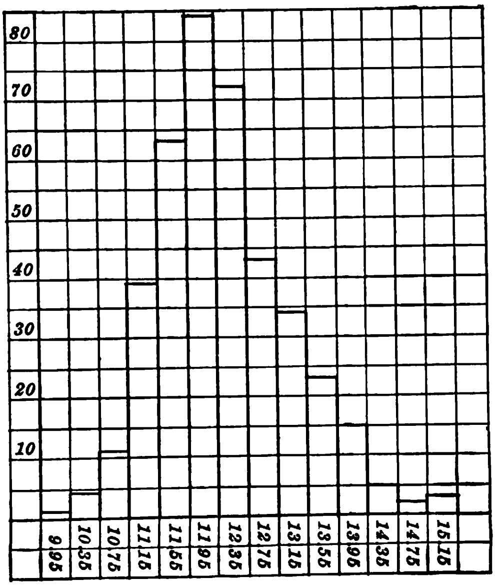


POLYGON No. 1L.

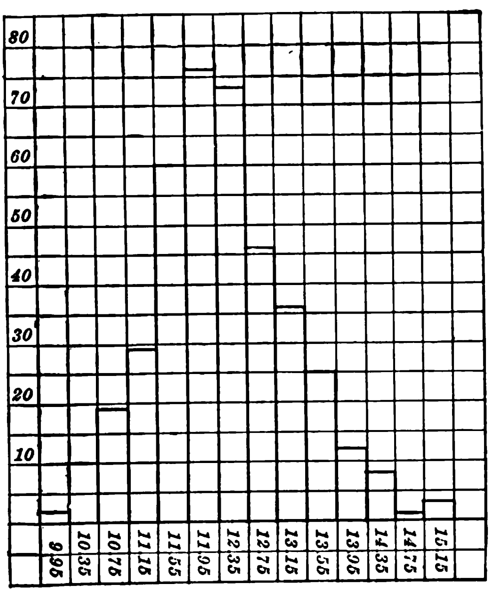
were collected at three different times (75 July 24, 125 August 17, and 200 August 24), of which the first and last were separated by over three weeks, this is not improbable. But as I have no data on ecdysis, it is impossible to settle this point.

2. *Median length.* This is the second largest dimension taken. It is slightly more variable than the frontal breadth. The polygons No. 2R and 2L represent similar distributions, with a greater frequency, however, at the mode of the Rights, as in the frontal Breadth, indicating less variability than in the Lefts.

3. *Right margin.* It should be remembered that No. 3R and 3L are not strictly comparable because of the asymmetry of the animals. The polygons have been placed together because they represent identical measurements. Comparison should also be made of No. 3R with 4L, the polygons for the margin on the side of the great chela of the Rights and

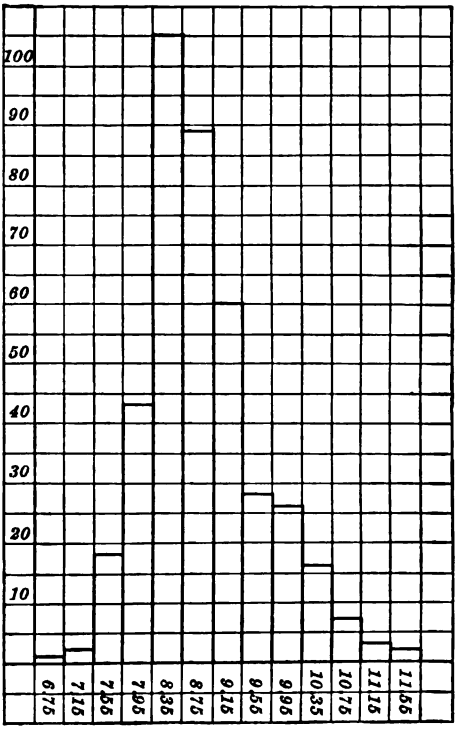


Polygon No. 2R.

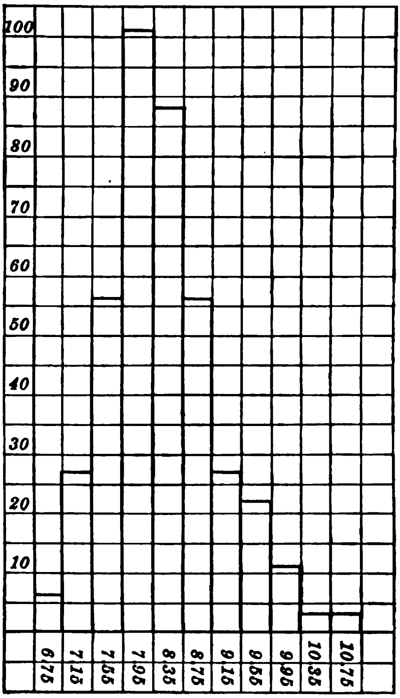


Polygon No. 2L.

Lefts respectively. No. 3R differs from 3L in having greater modal frequency and more classes; it differs from 4L by much greater modal frequency. As compared with the left margin the right is somewhat less variable. For both Rights and Lefts the margin on the side of

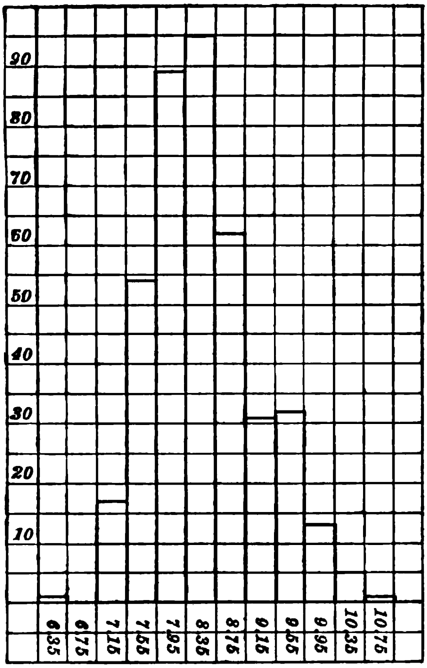


Polygon No. 3R.

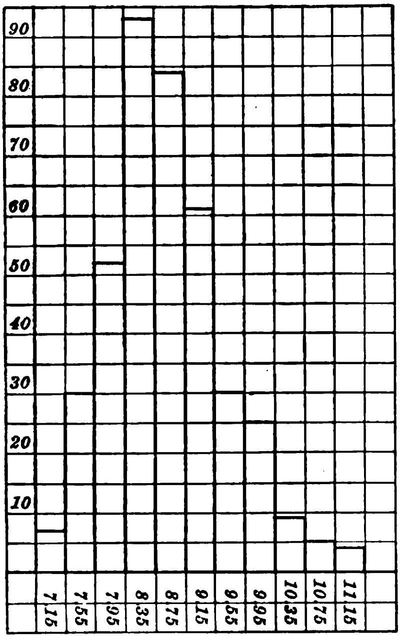


Polygon No. 3L.

the small chela is 5% shorter than the other. In the case of the Rights, 8.400 (Left) ÷ 8.842 (Right) = .9500, *i. e.* Left is 95% of Right. And for the Lefts 8.285 (Right) ÷ 8.716 (Left) = .9505, *i. e.* Right is 95+ % of Left. All dimensions are considerably larger on the side of the great chela, a fact which will be discussed later in connection with the problem of right- and left-handedness.

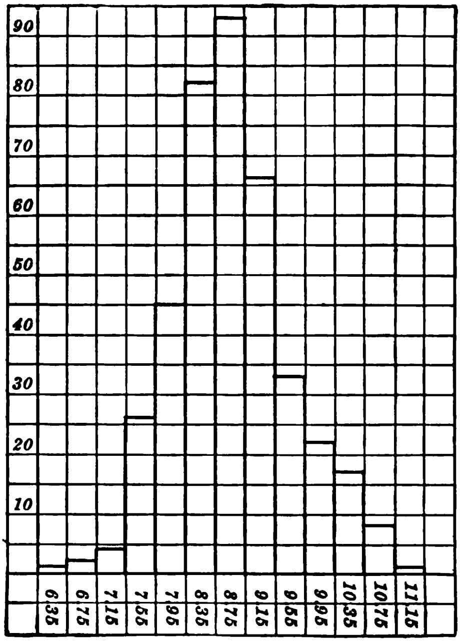


POLYGON No. 4R.



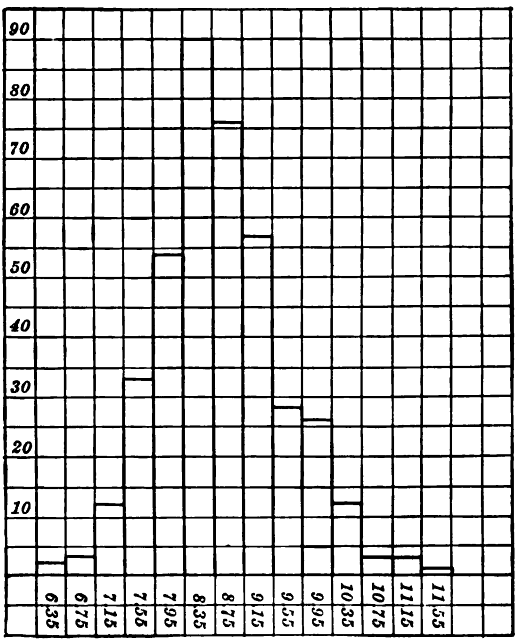
POLYGON No. 4L.

4. *Left margin.* Polygons No. 4R and 4L. Compare also No. 4R with 3L. The three dimensions thus far considered are the most valuable for place-mode determinations because they are expressive of the form of the carapace and may be measured with ease and accuracy. As given in Table I., the modal classes of the Lefts, — in two instances, — the frontal breadth and right margin, are below those of the Rights; in both of these cases there is considerable difference in the means.

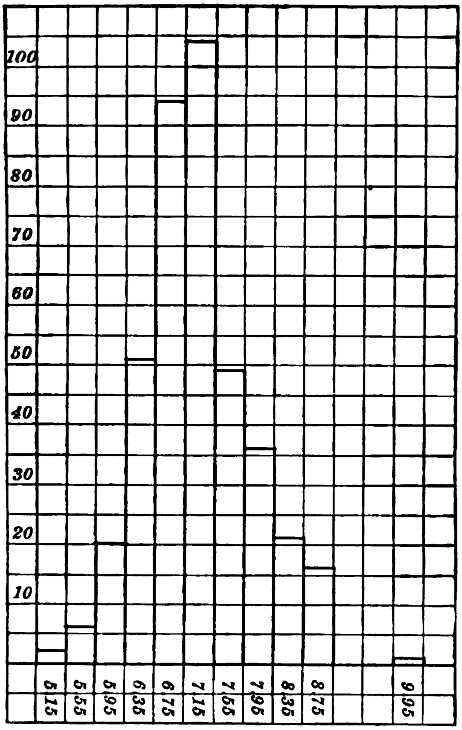


POLYGON No. 5R.

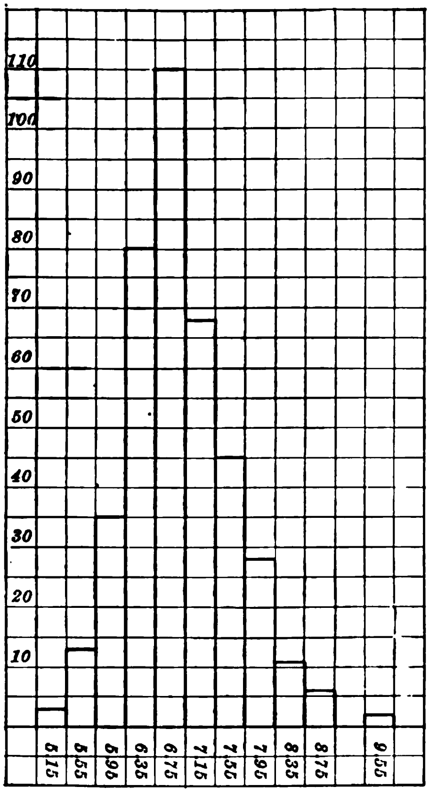
5. *Meropodite of great chela.* I shall here consider homologous organs. With the exception of the usual greater frequency of the modal class of the Rights, the polygons No. 5R and 5L are very similar. The difference in the coefficients of variability between the Rights and Lefts is .657 in favor of the Rights.



POLYGON No. 5L.



POLYGON No. 6R.



POLYGON No. 6L.

6. *Carpopodite of great chela.* Here we meet an exception in the matter of modal frequency, for the Lefts' mode contains more individuals than that of the Rights. No. 6R and 6L are otherwise similar. In comparison with the meropodite the carpopodite is much more variable.

Bateson ('94, p. 79), in his book on meristic variations, states that terminal members of a series are likely to be most variable. "In such cases as that of the last rib of Man, and several other animals, the wisdom teeth of Man, etc., it is quite true that in the terminal member Variation is more noticeable than it is in the other members." But such series as those of teeth and ribs, in which there is repetition of similar organs, are so different from the linear series of joints with which we are dealing, as to make inferences from one to the other unwarrantable.

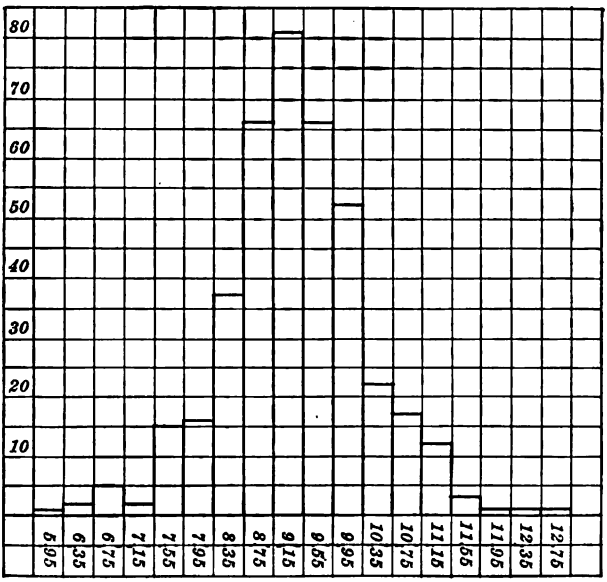
Bateson does mention (p. 63) substantive variation in the joints of the leg of the cockroach (Blatta americana), but only in its relation to the number of joints, no light being thrown upon our problem.

In case of the series of joints of the crab leg it would seem probable that the distal would be the most variable, since they are most likely to be modified by the use of the leg.

For convenience of comparation the Coefficients of Variablity of the measurements taken on the chelar joints are here repeated (see Table II.).

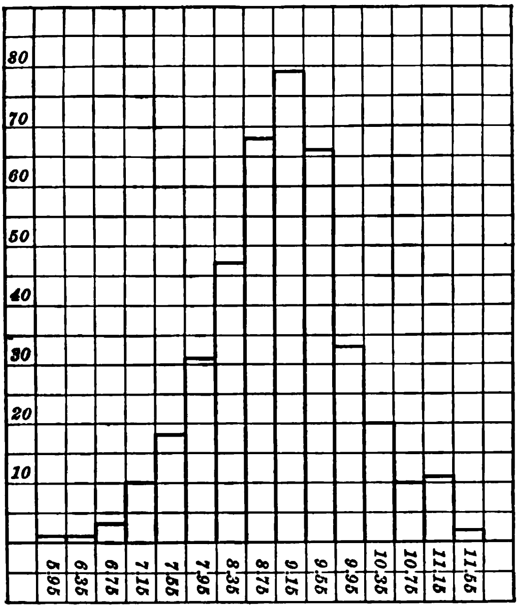
	Rights.	Lefts.
Meropodite of great chela,	9.000	9.657
Carpopodite of great chela,	10.166	10.472
Propodite of great chela,	10.215	10.255
Meropodite of small chela,	8.734	9.920
Carpopodite of small chela,	9.518	11.139
Propodite of small chela,	8.313	8.898

Only for the great chela of the Rights is there a constant increase in variability from the proximal to the distal joint. In every case, however, the carpopodite is much more variable than the meropodite.



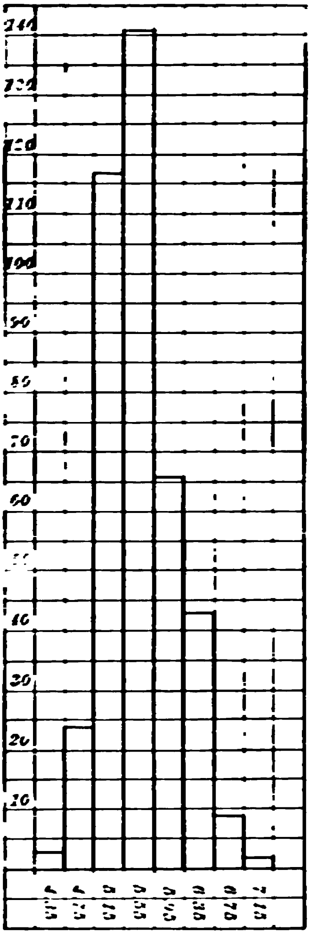
Polygon No. 7R.

Among the hundreds of crabs examined not a single variation in the number of joints was noticed.

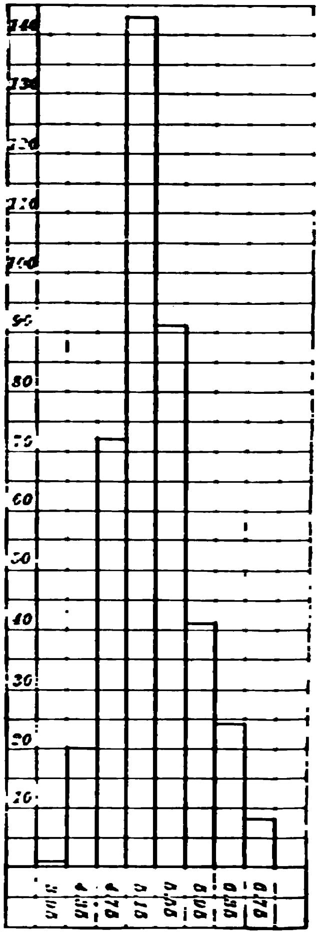


POLYGON No. 7L.

7. *Propodite of great chela.* Polygons No. 7R and 7L are more nearly symmetrical than any of those already examined; 7R has a slightly wider range of variation.

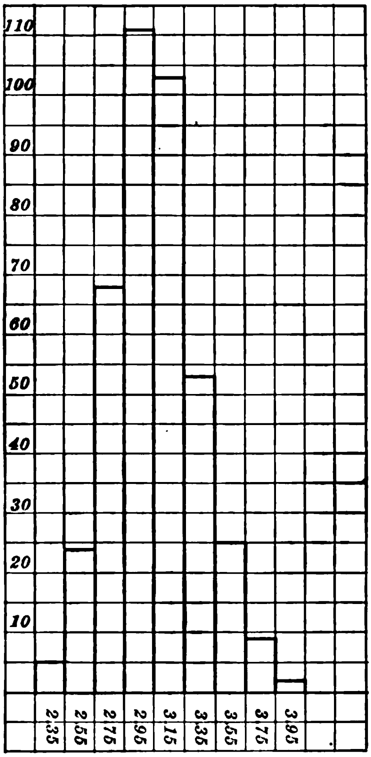


Polygon No. 8R.

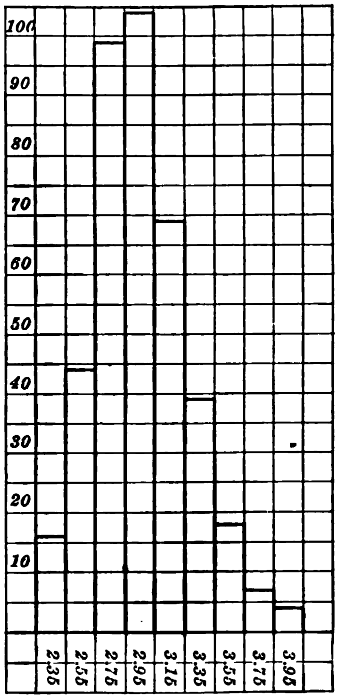


Polygon No. 8L.

8. *Meropodite of small chela.* Polygons No. 8R and 8L.

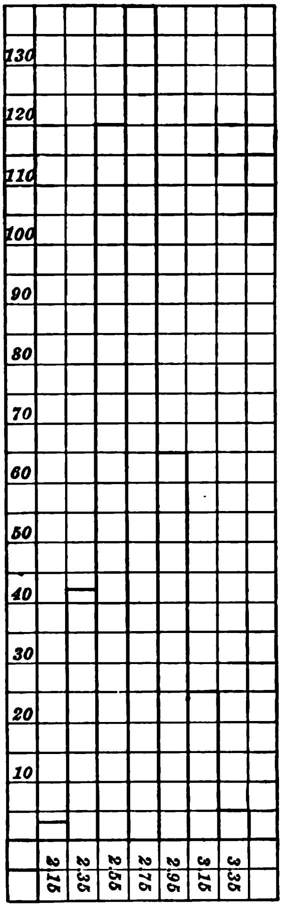


POLYGON No. 9R.

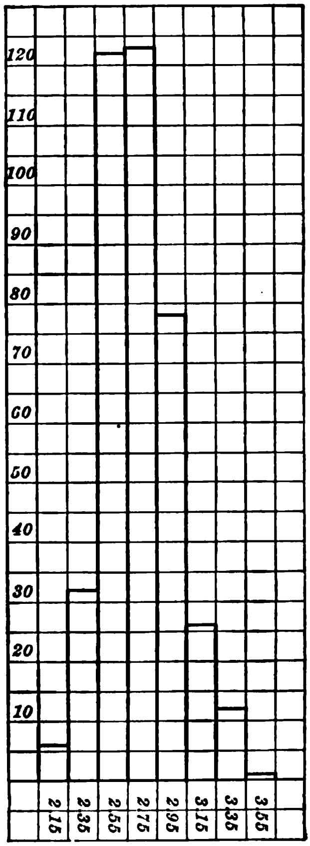


POLYGON No. 9L.

9. *Carpopodite of small chela.* Polygons No. 9R and 9L. The carpopodite is the most variable organ measured, the largest coefficient of variability being that of the carpopodite of the small chela of the Lefts, and the second largest, that of the carpopodite of the great chela of the Lefts.

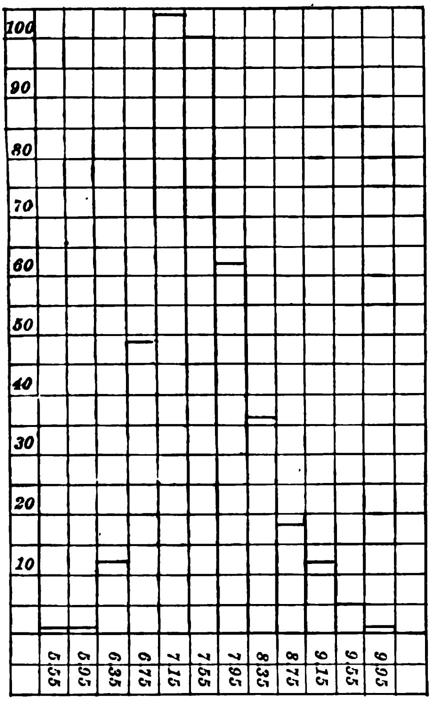


POLYGON No. 10R.

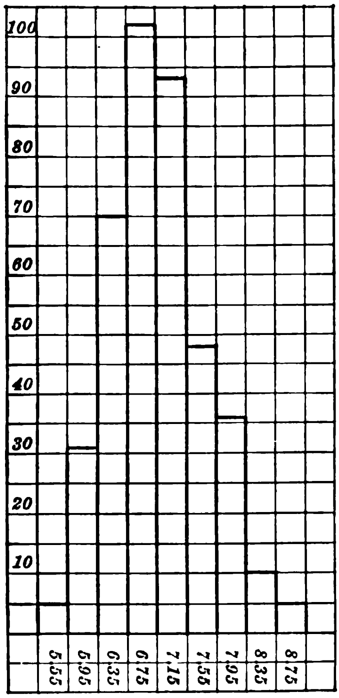


POLYGON No. 10L.

10. *Propodite of small chela.* Polygons No. 10R and 10L. The propodite of the small chela of the Rights is absolutely the least variable of the measurements made on the legs, while the propodite of the great chela of the Rights (Polygon No. 7R) is the most variable of all the organs of the Rights. We have here an illustration of Darwin's law, that a part (the propodite of the great chela) developed to an extraordinary degree is more variable than a part (the propodite of the small chela) of ordinary size. This law of variation holds for all the measurements on the great and small chelae of the Rights.

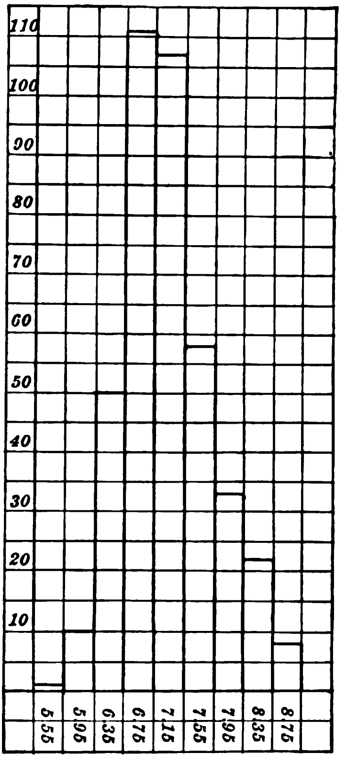


Polygon No. 11R.

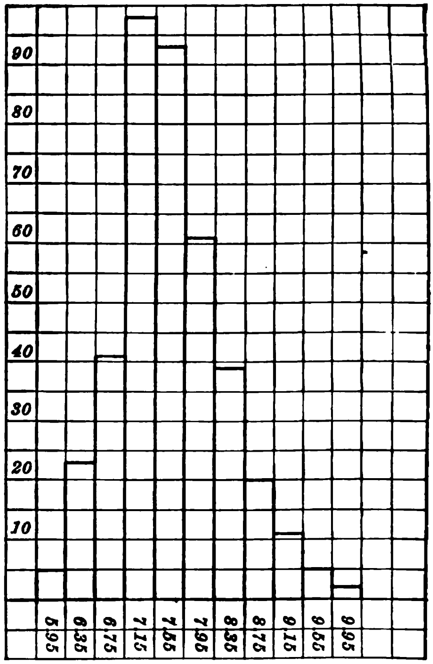


Polygon No. 11L.

11. *Meropodite of second leg on side of great chela.* Polygons No. 11R and 11L.



Polygon No. 12R.



Polygon No. 12L.

12. *Meropodite of second leg on side of small chela.* Polygons No. 12R and 12L. Attention may be called to the fact that in both Rights and Lefts the meropodite on the side of the great chela is larger than that of the opposite side. This apparently indicates that the influences which determine the development of the great chela affect other parts of the body as well.

4. *Table of Correlation of Meropodites of Chelae.*

In Table V. the correlation of the meropodites of the chelae of the left-handed animals is shown. This was determined in order to see whether there was not an inverse correlation; for it seemed not improbable that an unusually large Great Chela should be accompanied by an exceptional small Small Chela. Such, however, is not the case; instead there is a fairly close direct correlation, 0.774+.

TABLE V. — Correlation of Meropodites of Chelae of 400 Left-Handed Animals.

Relative Classes.		3.95	4.35	4.75	5.15	5.55	5.95	6.35	6.75	No. of Individuals.	Mean of Relatives.	Deviation from Mean.	Deviation of Relatives ÷ S. D. of Rel (0 527) A.	Deviation of Subject ÷ S. D. of Subject. (0.883) B.	A ÷ B.
Deviations of Relatives from Mean (= 5.31).		−1.36	−.96	−.56	−.16	+.24	.64	+1.04	+1.44						
Subject Classes.	Deviations of Subject from Mean (= 8.65).														
6 35	−2.30		2							2	4.35	− .96	−1.821	−2.751	+ .66
6.75	−1.90	1	2							3	4.22	−1 09	−2.069	−2.272	+ .91
7.15	−1 50		5	4	1	2				12	4.75	− .56	−1.062	−1.794	+ .59
7.55	−1.10		5	24	3	1				33	4.75	− .56	−1.062	−1.316	+ .80
7.95	− .70		3	22	24	1	2	2		54	5.02	− .29	− .550	− .837	+ .66
8.35	− .30		3	16	60	11				90	5.10	− .21	− .399	− .359	+1.11
8.75	+ .10			6	40	24	3	1	2	76	5.34	+ .03	+ .057	+ .120	+ .48
9.15	+ .50				12	37	7	1	0	57	5 58	+ .22	+ .417	+ .599	+ .70
9.55	+ .90				2	13	11	1	1	28	5.75	+ .44	+ .835	+1.080	+ .77
9.95	+1.30				1	2	16	7	0	26	5.89	+ .58	+1.100	+1.555	+ .71
10.35	+1.70						2	9	1	12	6.32	+1.01	+1.917	+2.084	+ .95
10.75	+2.10							2	1	3	6.48	+1.17	+2.221	+2.512	+ .88
11.15	+2.50							1	2	3	6.62	+1.31	+2.474	+2.990	+ .83
11.55	+2.90								1	1	6.75	+1.44	+2.730	+3.469	+ .79
No. of Individuals		1	20	72	143	91	41	24	8	400	Coefficient of Correlation . . .				.774+

V. *Discussion of Results.*

Concerning the original purpose of this study, the determination of some place-modes for the Fiddler Crab, it may he said that a number of modes have been given in Table I., which it is hoped will be of value in the future as helps in the study of racial variation and of the formation of species. As before remarked, those measurements which would seem the most valuable for place-modes are: (*a*) the frontal breadth, (*b*) the median length, (*c*) the right marginal length, and (*d*) the left marginal length.

It remains to be asked, What answers do the results of this study enable us to give to the group of questions centring about the Great Chela condition, with which we set out? (1) What is the significance of right- and left-handedness? (2) What relation does the size of the great chela bear to other dimensions? (3) What determines right- and left-handedness?

The chief significance of the great chela, observation leads me to conclude, is in its value (1) as a means of defence and offence, and (2) as a means of burrowing. But granting that these are sufficient reasons for its existence, we have still to ask why it is sometimes on the right side, sometimes on the left. The fact that approximately equal numbers of Rights and Lefts are found, seems to indicate that the great chela is not determined by heredity, or, at least, not directly. For if this were the case, the probability of an equal distribution between the two types would be very slight. It is more likely, therefore, that we are dealing with what is usually called (although improperly) a chance determination; that is, there are a number of variable factors, only partially known at present, which throw the great-chela-developing-tendency now this way, now that. Other instances of determination of this kind are the determination of sex and of the crossing of the optic nerves. Professor G. H. Parker, who has studied the crossing of the optic nerves of fishes, but whose results have not yet been published, has found that many symmetrical fishes are about equally divided between those having the right nerve crossing above the left and those having it crossing below the left. Since it is at present impossible to point out, in such cases, any uniform cause or group of causes for the condition, we say it is a matter of chance.

In answer to the second question, — What relation does the size of the great chela bear to the other dimensions? — it may be said, that the measurements which allow of comparison of the two sides of the body, namely,

the margin and the meropodite of the second leg, are larger on the side of the great chela. Expressed in percentages, the relations are as follows: Margin on chelar side in case of Rights, 5% greater than on opposite side, — the same is true of the Lefts; meropodite of second leg on chelar side in case of Rights, 6% greater than that of the opposite side; meropodite of second leg on chelar side in case of Lefts, 8% greater. The fact that measurements are greater on the chelar side may be taken in support of (*a*) the idea of chance determination, for any advantage of one side of the body over the other would be likely to affect all organs. On the other hand it may be held (*b*) that the development of the great chela is itself the cause of the greater development of the other organs on the same side. Or, combining these two views, it might be maintained (*c*) that the causes which led to the development of the great chela were operative also in case of the other organs, but that the development of the great chela was an additional cause for the unusual size of the other organs.

As to the difference in size of the Rights and Lefts I can only say that it is an interesting and surprising fact, for which I have found no explanation. I at first interpreted the fact that the Lefts are the smaller and the more variable as meaning that the Rights represented the stable form; and in support of this I had, as a result of the first summer's work (see Table III.), evidence that there were more Rights than Lefts. But this conclusion was not confirmed by the additional observations made during the summer of 1900 (see Table IV.). It may be, however, that the proportion of right- and left-handed animals varies in different colonies, and that during the interval between the collection of the animals referred to in Table III. and those of Table IV. migration or some other change had caused alteration in the relative frequency of Rights and Lefts; but this does not seem very probable.

VI. *Summary.*

1. The place-modes for twelve measurements on the carapace and extremities of right- and left-handed Gelasimus pugilator are given in Table I.

2. The means of Table I. show that the right-handed animals are larger and less variable than the left-handed.

3. Right- and left-handed animals occur in approximately equal numbers.

4. Two "stages" appear to be represented by the individuals measured. Many of the curves are compound, and it is probable that in these one mode represents those individuals which have recently molted, the other those which are almost ready for the process.

5. All the measurements are larger on the side of the great chela.

6. The results of this study in variation seem to indicate that right- and left-handedness is not directly due to heredity, but is caused by certain slight variations which give one side of the body an advantage over the other.

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CONTRIBUTIONS FROM THE ZOÖLOGICAL LABORATORY OF THE MUSEUM OF COMPARATIVE ZOÖLOGY AT HARVARD COLLEGE, UNDER THE DIRECTION OF E. L. MARK. — No. 122.

THE DEVELOPMENT AND FUNCTION OF REISSNER'S FIBRE, AND ITS CELLULAR CONNECTIONS. A PRELIMINARY PAPER.

By Porter Edward Sargent.

With Two Plates.

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THE DEVELOPMENT AND FUNCTION OF REISSNER'S FIBRE AND ITS CELLULAR CONNECTIONS. A PRELIMINARY PAPER.

By Porter Edward Sargent.

Presented by E. L. Mark, March 13, 1901. Received March 15, 1901.

In a recent number of the Anatomischer Anzeiger (Bd. XVII. pp. 33–44) I have described the occurrence of Reissner's fibre in the canalis centralis of vertebrates, and I there promised the early appearance of a paper on its development. My further researches on its development and cellular connections have led to the discovery of a highly specialized apparatus, of which the so-called fibre forms a part. The subject has developed much larger aspects than was anticipated, and the consequent delay in the publication of my complete results makes necessary a further preliminary paper.

As described in the previous paper, Reissner's fibre lies in the cerebro-spinal fluid; it extends through the whole length of the canalis centralis and the brain ventricles to the anterior portion of the optic lobes, where it passes into the brain tissues; it gives off throughout the posterior portion of its course fine branches, which enter the tissue of the spinal cord.

In the present paper I hope to show briefly that there is normally in the central nervous system of all vertebrates a highly specialized apparatus, the cells of which lie in the optic lobes and send their axons into the optic ventricle and the central canal to form the so-called Reissner's fibre. I have investigated the occurrence of this apparatus in upwards of one hundred species, representing all the principal classes and subclasses of vertebrates. The development has been studied in about twenty different species, and has been more or less completely worked out in representatives of all the chief groups of vertebrates. In this paper I shall describe the apparatus and its development in a few char-

acteristic forms, reserving the more detailed account of the investigations for a later and more extended article.

In *Amia,* at about the time of hatching, there is in the anterior portion of the roof of the third ventricle a differentiation of the neuroblasts. Some of them have already increased in size, have become more nearly spherical and take the stain more deeply than the surrounding cells (Figure 1). These enlarged cells are concentrated for the most part in the median plane at the anterior end of the tectum opticum near the posterior commissure. During the first stage of differentiation there are from twenty to thirty of these cells, but by the development of indifferent neuroblasts they increase rapidly in number, so that by the end of the fourth day after hatching there are from eighty to one hundred of them. During the first day the tectum is only one cell thick. Each cell has a large nucleus — whose diameter is somewhat more than one half that of the cell — with a single deeply staining nucleolus.

During the first and second days the axons develop from the cells as extremely fine processes, which always appear on the side of the cell nearest the ventricle, directly towards and into which they grow. Early in the third day adjacent axons, now projecting into the ventricle, come together in groups and coalesce at their tips (Figure 2), appearing as a single fibril in their further growth through the cerebro-spinal fluid. In later stages these fibrils coalesce with others similarly formed, and in their growth backwards through the fluid of the ventricles and canal form what has been known as Reissner's fibre (Pl. 2, Figure 8.) During larval development the fibrils which make up Reissner's fibre coalesce more and more, until by the eighth day there are only six or eight separate divisions of the fibre in the ventricle, and later these are still further reduced in number by further coalescence. The cells also give off dendrites, which run backward through the substance of the tectum.

In the later development of the tectum opticum these cells undergo an apparent migration, due to the development of intervening tissue, as a result of which their relative positions are considerably changed; the cells become more crowded together. During these changes in position the axis of the cell may rotate through an arc as great as 180°. It is an interesting fact that the eccentric nucleus always retains its position at the side of the cell opposite that from which the axon emerges.

At about the time of hatching one may find in the extreme posterior end of the canalis centralis (Figure 5) a number of small cells, three to four micra in diameter, lying in the lumen of the canal and ventriculus

terminalis. The surrounding walls of the canal are made up of a single layer of cells, actively dividing. Certain of these cells become separated from the walls and pushed into the lumen. Of these many atrophy and disintegrate. Some eight to twelve of them persist and continue to develop. These cells, at first spherical, become spindle-shaped, as they increase in size. These posterior canal cells (as I temporarily call them) give off peripherally a number of dendrites which penetrate the tissue of the cord (Figure 3). From the tapering anterior end of the cell is given off the axon (Figure 4), which runs cephalad through the lumen, eventually coalescing with the axon of similar cells (Figure 5) and then continuing its growth cephalad. About the third day this system of forward-growing axons meets the system of axons from the cells of the tectum growing backward and the two systems coalesce in a way not yet clearly made out, to complete what has been called Reissner's fibre. This fibre, then, is a nerve tract, composed of axons running in opposite directions, both cephalad and caudad. The development of this apparatus as outlined for Amia is typical of all vertebrates.

The condition of the apparatus in *Selachii* is especially interesting. In the skate Raja erinacea the cells are of great size ($25\,\mu$ to $30\,\mu$ in diameter), being the most conspicuous elements in the brain. They are three hundred to four hundred in number, and lie in two bands, one on either side of the median plane, extending the whole length of the roof of the optic lobe (Pl. 2, Figure 9). At the anterior end these two bands meet, forming a large group of closely aggregated cells. The cells are multipolar, giving off several processes in addition to the large axon, which is $2\,\mu$ to $3\,\mu$ in diameter. As in Amia, the nucleus is eccentric, being always at the side of the cell opposite that from which the axon emerges. The number of the capillaries in the neighborhood of these cells, supplying them with blood, gives evidence as to the extent of the activity of the cells.

Although these cells are so conspicuous in the brain of the skate, they have attracted but little attention. They were first seen by Rohon in selachians and correspond in position to the "Dachkerne" which have been described for Amphibians and Reptiles, the function of which has not been established.

The axons pass dorsad and laterad from their cells, turning either cephalad or caudad, and form two great tracts of non-medullated fibres of large size, which extend through the whole tectum opticum lateral and dorsal to the cells. The fibres running caudad can easily be traced to the posterior end of the tectum, whence they pass into the cerebellum

and come into close proximity to the Purkinje cells. The fibre tract which runs forward may be traced to the anterior end of the tectum, where the fibres converge, apparently forming Reissner's fibre, which emerges from the tectum into the ventricle at this point. Where Reissner's fibre leaves the brain tissue, the membrane covering of the roof of the ventricle is continued in a cone-like projection surrounding the fibre (Figure 9). Still another process given off from these cells passes peripherad nearly to the outer surface of the tectum, where it comes directly in contact with the endings of the optic nerve fibres. These cells, whose axons form Reissner's fibre, are, then, in direct connection with the eye through the optic nerve, and in turn are connected with the Purkinje cells of the cerebellum, which are known to coördinate muscular movements. The posterior canal cells in the selachians are of relatively large size and about a dozen in number.

In the *Cyclostomata* this apparatus is in a more primitive condition. In Petromyzon marinus it begins to develop some time after hatching, and is not fully established until the second month of larval life. In larvæ thirty days after hatching the cells form a small but well-marked group lying in the roof of the rudimentary optic lobes in the median plane, and occupying the whole thickness of the tectum (Figure 7). The axons emerge directly into the optic ventricle and unite in groups to form Reissner's fibre. These axons may continue backward to the fourth ventricle in three or four separate divisions, but in later development these coalesce more and more. At this stage the posterior canal cells are already developed and are sending their axons cephalad through the canal, but they have not yet united with the axons of the tectal cells running caudad.

In the adult Petromyzon Reissner's fibre passes through the canalis centralis and the fourth ventricle, from which it enters the brain tissue of the basal portion of the cerebrum and passing through this emerges into the third ventricle. Here it breaks up into several trunks and continues forward to the anterior portion of the ventricle, where after further division it enters the tectum.

The passage of Reissner's fibre for a portion of its course through the nervous tissue in cyclostomes is especially interesting as throwing light on a little understood structure in Amphioxus. Of the dorsal colossal nerve cells in the anterior portion of the central nervous system of Amphioxus, the largest and most anterior, designated by Rohde as the "kolossale ganglien-zelle," is median and lies across the lumen of the canalis centralis. The cell is in direct connection with the pigment spot.

The axis cylinder runs caudad in the median plane just ventral to the floor of the canal. I venture the conjecture that this cell represents, in Amphioxus, the tectal cells of craniotes, and that its giant axis cylinder is homologous with Reissner's fibre. In the phylogeny of this apparatus the cyclostomes would then furnish the connecting link between Amphioxus and the gnathostomes.

A number of experiments have been performed to determine the functions of this apparatus. The best results have been obtained with dogfish (Squalus acanthias), and small sharks (Charcarias littoralis). In these animals Reissner's fibre is of such size (10 μ to 20 μ in diameter) that it is possible to remove portions of it from the brain ventricles or canal for microscopical examinations. The operation of breaking the fibre

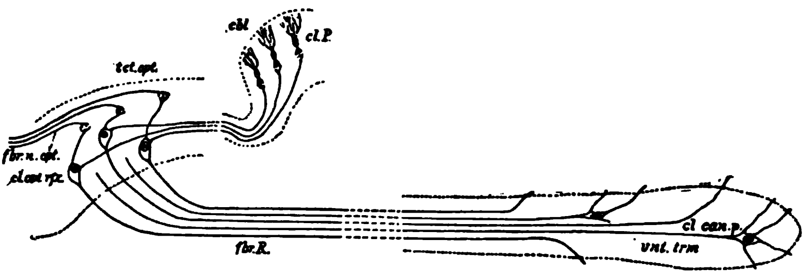


FIGURE *A*. Diagram of the optic reflex apparatus. *cbl.*, cerebellum; *cl. can. p.*, posterior canal cells; *cl. opt. rfx.*, optic reflex cells; *cl. P.*, Purkinje cells of cerebellum; *fbr. n. opt.*, afferent optic nerve fibres; *fbr. R.*, Reissner's fibre; *vnt. trm.*, ventriculus terminalis; *tct. opt.*, tectum opticum.

was easily performed. By an incision through the integument, and the removal of a small bit of cartilage, the tela choroideus covering the fourth ventricle was exposed. Through this a curved needle was plunged, and drawn several times transversely across the ventricle to break the fibre. The wound was then dressed; the animal, when replaced in the water, usually recovered from the shock in from twenty to thirty minutes. Those individuals in which the operation had been performed without success in breaking the fibre, served for the control experiments. The success or failure was ascertained at the autopsy, performed at death or on the fourth or fifth day after operation. Furthermore, the cord and medulla of each individual was preserved for microscopical examination. In about one third of the cases the operation had failed to

break the fibre. These individuals showed a marked difference in behavior from those in which the fibre had been broken. The former, after recovery from shock, were apparently normal in their reactions. Those in which the fibre had been broken showed a slowness in response to optical stimuli. For example, such an animal, in swimming about the tank in which it was confined, would bump into the sides of the cage. If any obstacle were suddenly placed in front of it while swimming, its effort to avoid the obstacle would come apparently too late to prevent collision. Those individuals in which subsequent autopsy and examination showed the fibre to be intact exhibited much greater dexterity and quickness in avoiding obstacles. The behavior of the animals operated on was constantly compared with normal individuals kept with them in the same enclosure. These experiments could be made entirely conclusive only by comparing the time reactions in cases where the fibre was cut with those where it remained uncut. No attempt has yet been made to do this.

The apparatus which is the subject of this paper forms, I believe, a short circuit between the visual organs and the musculature, and has for its function the transmission of motor reflexes arising from optical stimuli. This view as to its function is supported by many distinct lines of evidence, which are here classified and summarized.

(1) *Anatomy*. There is normally in all vertebrates a group of cells lying in the optic lobes which by some of their processes are in direct connection with the central terminations of the optic nerve, and by others with the Purkinje cells of the cerebellum. Their axons pass by the shortest route through the ventricles and canal to the posterior portion of the nervous system, where they pass into the cord and probably out through the ventral roots to the musculature. These anatomical connections make it probable that this apparatus is a direct path for the transmission of motor reflexes arising from optical stimuli. The connection with the Purkinje cells of the cerebellum, it is equally evident, is for the coördination of muscular movements.

(2) *Experimental Physiology*. When Reissner's fibre is cut or broken, the animal loses the power of responding quickly to optical stimuli. This is not due to the shock resulting from the operation, for animals on which the equivalent operation has been performed without breaking the fibre are nearly or quite normal in this respect.

(3) *Comparative Physiology*. (*a*) In any one group, as for example the teleosts, the apparatus has its highest development in those animals which are most active. In the predatory and rapacious bluefish (Poma-

tomus) the apparatus is highly developed, Reissner's fibre having a diameter of 10 μ. In Lophius, which is a much larger fish, but is usually sedentary and quiescent in its habits, and more dependent upon tactile than visual sensations for obtaining its food, the apparatus is degenerate and Reissner's fibre inconspicuous. (*b*) The corpora quadrigemina in higher vertebrates are degenerate organs, having given up most of their functions to other parts of the brain. In mammals they are, it is generally believed, concerned only with reflex functions. Assuming this to be true, the apparatus under discussion, since it has its centre in the corpora quadrigemina, must have, in the higher vertebrates at least, a purely reflex function.

(4) *Embryology.* (*a*) The apparatus does not reach full development until just before the animal attains free life. In the active fry of trout and salmon, which give reflex responses at this early age, it is fully developed at the time of hatching. In those forms in which the young are retained within the uterus of the mother until a late stage of development, as in mammals and some selachians, the apparatus is not developed until a relatively much later stage. (*b*) In sluggish larvæ the apparatus is not established until after the time of hatching; in Amia not until the fourth or fifth day, in Petromyzon not until the second month. This corresponds closely with the time at which these larvæ begin to respond promptly to definite optical stimuli from surrounding objects. (*c*) In those mammals which are born blind, as the mouse and kitten, the apparatus at birth is in a very incomplete state, so that it cannot be functional. In the mouse at birth the axons are just penetrating into the ventricle, and Reissner's fibre is as yet unformed.

(5) *Degeneration.* A study of the blind vertebrates of the cave fauna from the collections of Professor C. H. Eigenmann show that the optic reflex apparatus is reduced in direct proportion to the degeneracy of the eye. In those species which are totally blind no trace of this apparatus is to be found.

Experiments are now in progress to determine the effect of artificial extirpation of the eye on this apparatus.

Such a "short circuit" for the transmission of optical motor reflexes must be of great importance in saving time. If the impulse were transmitted from the termination of the optic nerve to the posterior musculature through the cord, it would involve transmission through a chain of from two to three neurons. Now, it is well known to psychologists that the time of transmission of a nerve impulse is delayed by passing through

a cell body, and by passing from one neuron to another. Wundt found that the delay in the spinal ganglion cell of man was 0.003 second. The delay in passing between different neurons is probably greater, say 0.005. So in man, if two cell bodies and two contacts between separate neurons are to be traversed, the loss of time would be ($[0.003 \times 2] + [0.005 \times 2] =$) 0.016 second. In lower animals, as is well known, the time reactions are much greater. It is quite probable that in some of the lower animals this short circuit may mean the saving of a considerable fraction of a second.

An animal suddenly confronted with some optical evidence of danger from which it recoils in fear, does so reflexly, calling into operation this apparatus. When we pause to consider how often in the struggle for existence the saving of a fraction of a second may be a question between life and death, we see how important a part this apparatus may have played throughout the vertebrate series in the survival of the fittest.

EXPLANATION OF PLATES.

ABBREVIATIONS.

cbl.,	Cerebellum.	*fbr. R.*,	Reissner's fibre.
cl. opt. rfx.,	Optic reflex cells.	*tct. opt.*,	Tectum opticum.
coms. p.,	Posterior commissure.	*vnt. III.*,	Third ventricle.
e'phy.,	Epiphysis.	*vnt. IV.*,	Fourth ventricle.

PLATE 1.

FIGURE 1. Amia calva, 1st day. Sagittal section (anterior end at right) through roof of mid-brain. The large cells in the tectum opticum are the tectal reflex cells, a few of which are just beginning to send out their axons.

FIGURE 2. Amia calva, 12th day. Sagittal section (anterior end at left) through anterior part of tectum opticum. The numerous fibrils entering the third ventricle are the axons of tectal reflex cells, a few of which are shown in the section, but the most of which are lateral to this section.

FIGURE 3. Amia calva, 6th day. Transverse section of the spinal cord through the ventriculus terminalis; posterior canal cell sending its dendrites through the fluid of the canal into the tissue of the cord.

FIGURE 4. Amia calva, 1st day. Sagittal section through the posterior end of the spinal cord and ventriculus terminalis, showing a single posterior canal cell, its long process directed cephalad.

FIGURE 5. Amia calva, 12th day. Sagittal section of a portion of the spinal cord near its posterior end; posterior canal cells in the ventriculus terminalis and canalis centralis, sending their axons forward to form Reissner's fibre. Reconstruction drawing from four successive sections.

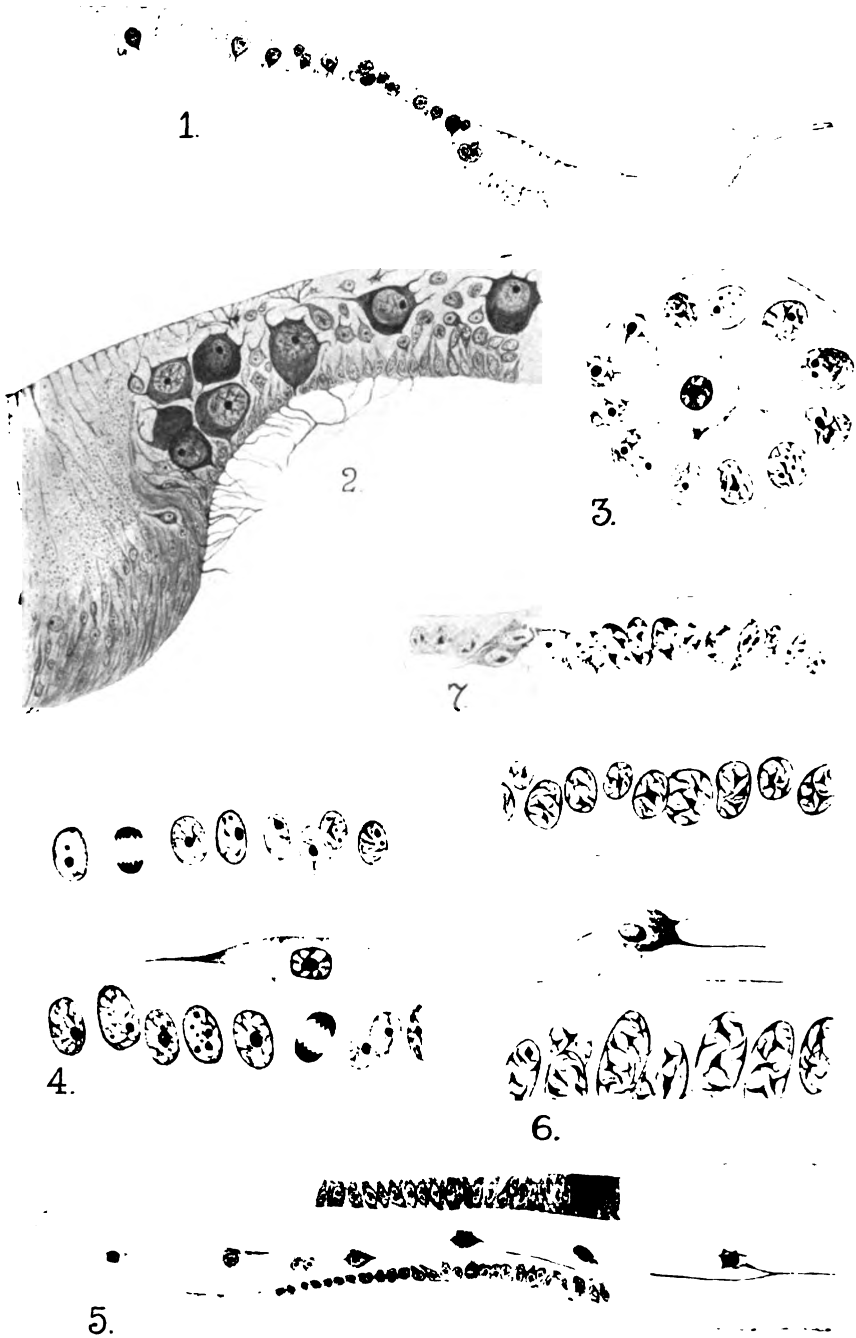
FIGURE 6. Squalus acanthias, embryo 2 cm. long. Longitudinal sagittal section. Posterior canal cells in the canalis centralis sending dendrites into the cord and its axon cephalad.

FIGURE 7. Petromyzon marinus, 30 days. Sagittal sections of the tectum opticum (anterior end to the right); the axons of the developing tectal reflex cells are just emerging into the third ventricle.

PLATE 2.

FIGURE 8. Amia calva, 12th day. Sagittal section through brain, somewhat diagrammatic.

FIGURE 9. Raja erinacea, 14 cm. long. Sagittal section of the mid-brain, diagrammatic.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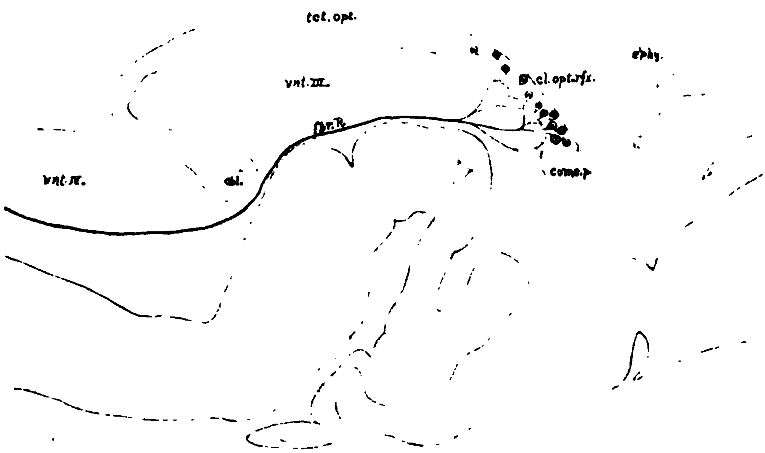
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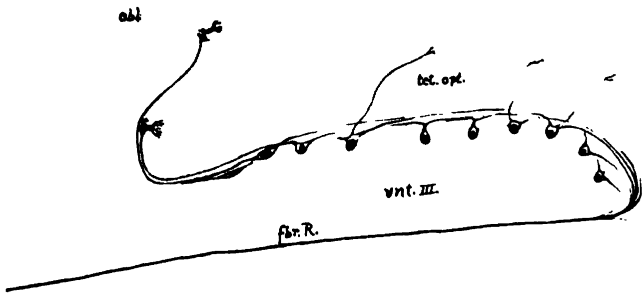
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CONTRIBUTIONS FROM THE GRAY HERBARIUM OF HARVARD UNIVERSITY.

NEW SERIES. — NO. XX.

BY B. L. ROBINSON.

I. Synopsis of the Genus *Melampodium*.

II. Synopsis of the Genus *Nocca*.

III. New Species and newly noted Synonymy among the Spermatophytes of Mexico and Central America.

CONTRIBUTIONS FROM THE GRAY HERBARIUM OF HARVARD UNIVERSITY, NEW SERIES, NO. XX.

By B. L. Robinson.

Presented March 13, 1901. Received March 16, 1901.

I. — SYNOPSIS OF THE GENUS MELAMPODIUM.

In the following key to *Melampodium* the genus is limited as by Bentham and Hooker in their Genera Plantarum and by Hoffmann in Engler & Prantl's Natürlichen Pflanzenfamilien. It will, therefore, be unnecessary here to reproduce the generic description or give generic synonymy. The key is based chiefly upon the material which has accumulated in the Gray Herbarium, including the recently acquired Klatt collection and some borrowed material from the U. S. National Museum. The writer has also in connection with this work been kindly permitted by Mr. Casimir de Candolle to examine and trace the types in the Prodromus Herbarium. Much difficulty has been experienced in giving the species a natural sequence, and after many efforts the hope of securing such an arrangement has been abandoned. The employment of pubescence in grouping the species of this genus is new and appears to yield more satisfactory results than an implicit reliance upon the fructiferous bracts. The latter, as is well known, often surpass the achenes, forming above them a cup or hood. This hood is often pointed dorsally at the summit and the point may be recurved or spirally coiled. Unfortunately, however, these features, the hood and its appendage, show too great variability in certain nearly related forms, such as *M. sericeum* and its varieties, to yield diagnostic characters of the first rank. However, the presence or absence of a hood can usually be determined readily, and the two sections *Eumelampodium* and *Zarabellia* may conveniently be retained.

Bentham and Hooker, l. c., estimated the species at eighteen, and Hoffmann, l. c., accords twenty-five species to the genus. It will be seen, however, that this number can, with our present knowledge, be somewhat increased. The genus reaches its greatest development in Mexico, where, if we include Lower California and Central America, no less than thirty-one species occur. Of these species three reach the southern United States (one merely as an introduction), two are found

in the West Indies, and two or three extend to South America. There are also two species known exclusively from South America. Early in the nineteenth century a species of *Melampodium* (*M. diffusum*) was discovered on the island of Luzon in the Philippines. As the genus is otherwise American, the occurrence of this species in a region so remote has always been problematic, and it has been a matter of no small interest to find the Philippine plant closely matched by specimens recently collected by Dr. Edward Palmer, about Acapulco, Mexico. There can therefore be scarcely a doubt that the genus is in reality of New World origin, and that a single Mexican species was accidentally introduced into the Philippines, where it attracted scientific attention before it was recognized in America. This seems the more likely from the circumstance that Mexico and the Philippines were under the same national control, and early connected by a certain amount of oceanic traffic. This being the case, the transference of seed from Acapulco, the most important Pacific port of Mexico, to the neighborhood of Manila, presents no inherent improbability. The writer is under obligation to M. Robert Buser of the De Candollean Herbarium for critical comparison, notes, and sketches relative to this and related species.

In this paper the term *fruit* is applied to the ray-achene and the closely enveloping bract.

§ 1. Eumelampodium, DC. Inner (fructiferous) bracts of the involucre exceeding the inclosed achene and developed at the summit into a cup or hood (this obsolete in some forms of *M. sericeum*). — Prodr. v. 518 (1836).

* Lower surface of the leaves sparingly pubescent to hirsute, villous, or tomentose, but not sericeous.

+ South American species: hoods scarcely or not at all appendaged.

++ Herbaceous annual: rays conspicuous, 6.5 mm. long, unguiculate.

1. M. paludicola, Taubert in Engl. Jahrb. xxi. 455 (1896). — Swamps on the Paranahyba River, Prov. Goyaz, Brazil, *Ule*, no. 2978. Not seen by the writer.

++ ++ Suffrutescent: rays very small, inconspicuous.

2. M. suffruticosum, Baker in Mart. Fl. Bras. iv. pt. 3, 162 (1884). On the Esmeralda plains of the upper Orinoco in S. Venezuela. A species omitted from the Index Kewensis. The achenes are crowned by a shallow cup, otherwise the plant would be placed next *M. camphoratum*, to which according to the original description it is presumably related.

+ + Species of Mexico and S. United States.

++ Rays short and inconspicuous: appendage of the hood elongated, recurved or coiled: heads usually (but not always) subsessile or short-peduncled.

3. M. LONGICORNU, Gray, Mem. Am. Acad. v. 321 (Pl. Thurb.), 1854, where by misprint *longicorne.* — S. Arizona, near Ft. Huachuca, *Lemmon*, no. 2777; Sonora, Santa Cruz, *Thurber*, no. 937 (type); Chihuahua, near the city, *Pringle*, no. 10; San Luis Potosi, *Parry* & *Palmer*, no. 443½.

↔ ↔ **Ligules longer, exceeding the involucral bracts, conspicuous: peduncles mostly long.**

= **Soft-stemmed, strictly herbaceous and annual.**

a. **Pubescence short, scanty: leaves oblong to linear, entire: appendage of the hood long: involucre gamophyllous about to the middle.**

4. **M. appendiculatum.** Slender, erect, sparingly pubescent annual, 3 to 4 or more dm. high, branched almost from the base: leaves thin, oblong to linear, attenuate at the apex, scarcely narrowed to the sessile subauriculate base: obsoletely serrate to quite entire, the larger ones (near the middle of the stem) 5 cm. long, 1 cm. broad: peduncles 2 to 7 cm. long, erect, slender: involucre saucer-shaped or shallowly cup-shaped, gamophyllous, the limb shallowly 5-lobed; the lobes rounded or barely and very obtusely pointed, their margins scarious: pubescence of the peduncles and involucres short and sparing: rays 8 to 10, oblong, yellow, 6 mm. in length, 2–3-toothed at the apex; fruit tuberculate, the conspicuous appendage a linear coiled awn from an ovate-lanceolate somewhat 2-toothed base: pales scarious. — Southwestern Chihuahua, *Dr. Edward Palmer*, no. 245 (collection of 1885). Type in herb. Gray. This species has the outer involucre of *M. cupulatum*, Gray, and the fruit of *M. longicornu*, Gray, yet it is clearly distinct from both, differing from the former not only in its long peduncles and well-developed ligules, but in stature and in the size of the leaves, and from the latter in the presence of a hood and appendage (both totally lacking in *M. cupulatum*) and in the subauriculate base of the leaves.

Var. **leiocarpum.** Similar in all points but the fruit smooth, striate, glandular-punctate, not at all tuberculate. — Collected by Dr. Edward Palmer at Alamos, 16–30 September, 1890, no. 726. Type in herb. Gray.

Var. **sonorense.** Involucre deeper, subcampanulate: fruit slightly roughened: otherwise like the type. — Collected by C. V. Hartman at Cochuto, Sonora, 2 October, 1890, no. 71. Type in herb. Gray.

b. **Pubescence short and stiff: leaves lanceolate, undulate: fruit hooded, but the appendage shorter or sometimes obsolete.**

5. **M. arenicola.** Decumbent or suberect, branching from near the base; stems dark purple, covered with stiff white somewhat reflexed

hairs: leaves lanceolate from a narrowed auriculate base, undulate to sparingly and irregularly scabrous-pubescent upon both surfaces, 3 to 5 cm. long, 8 to 11 mm. broad: peduncles slender, pubescent, 3 to 7 cm. long; heads often nodding, 1.2 cm. in diameter (including narrow yellow entire or bidentate ligules); involucre shallow, saucer-shaped, the 5 divisions united nearly to the middle, broad, scarious and ciliate at the margin: fruit finely striate, punctate and slightly tuberculate, bearing a well-developed hood surmounted by a slender recurved hispidulous appendage not flanked by lateral teeth at the base. — Collected by F. H. Lamb in sandy soil on Isla Piedra, Mazatlan, Sinaloa, 31 December, 1894, no. 361a. Mr. Lamb's no. 380 also from Mazatlan differs in having no tubercles upon the fruit and in the obsolescent appendage, yet it is probably of the same species. Type in herb. Gray.

c. Pubescence copious, soft, long, villous: leaves ovate-lanceolate to ovate: appendage of the hood short: involucre gamophyllous only near the base.

6. M. LONGIPILUM, Robinson. Involucre externally villous, its divisions acutish. — Proc. Am. Acad. xxvii. 173 (1892). — San Luis Potosi, *Pringle*, nos. 3639, 4537.

= = Stems tending toward lignescence: roots at least in part perennial: species of northern Mexico and southern United States.

a. Heads rather small, (including the rays) about 1 to 1.2 cm. in diameter: leaves conspicuously sinuate or pinnatifid: rays thin, short.

7. M. CINEREUM, DC. l. c. (1836). Hood muticous. — Laredo, Texas, *Berlandier*, who appears to have confused this with the variety *ramosissimum*, so that his numbers cannot be depended upon.

Var. RAMOSISSIMUM, Gray. Hood mucronate. — Syn. Fl. i. pt. 2, 239 (1884), in part. *M. ramosissimum*, DC. Prodr. v. 518 (1836). — Near Laredo, *Berlandier*, S. W. Texas and adjacent Coahuila, *Palmer*, nos. 556, 557, 558 (coll. of 1880).

Var. ARGOPHYLLUM, Gray. Hood muticous: leaves small, tomentose upon both surfaces, canescent above, snowy white beneath. — Gray in Wats. Proc. Am. Acad. xviii. 104 (1883 without description). — Coahuila and Nuevo Leon, *Palmer*, no. 2068 (coll. of 1880).

8. M. LEUCANTHUM, Torr. & Gray, Fl. ii. 271 (1842). — The commonest form of our southwestern States. Kansas, Hamilton County, *Hitchcock*, no. 250; W. Texas, *Lindheimer*, no. 636, *Reverchon*, no. 1380*, *Thurber*, no. 128, *Heller*, no. 1632, *Pope*, *Bigelow*, *Wislizenus*; New Mexico, *Thurber*, no. 1105, *Wooton*, no. 117; Arizona, *Rothrock*, no. 327, *Palmer*, no. 608, *Pringle*, coll. of 1884; Chihuahua, *Pringle*. This plant has of late been generally regarded as a mere form of

M. cinereum, DC. However, it differs conspicuously in its more entire erect or ascending thickish leaves, its much larger heads (nearly or quite twice as broad) and its long thickish, firm, persistent, and veiny rays. It is a much commoner and more widely distributed plant than *M. cinereum*, and may be conveniently regarded as a specific type.

* * Lower surface of the leaves silky-villous, the pubescence more or less flocculent and tending to be deciduous.

+ Ligules shorter than or about equalling the fructiferous bracts: heads sessile or short-peduncled.

9. M. SERICEUM, Lag. Hoods tipped by a slender recurved appendage. — "Elench. Hort. Madr. 1805," Gen. et Spec. Nov. 32 (1816); DC. Prodr. v. 518; not HBK. — Mexico, *Mendez;* Oaxaca, *Pringle*, no. 6728; Durango, *Rose*, no. 3476; Jalisco, *Rose*, nos. 2819, 3561; Esperanza, *Dugès*.

Var. **exappendiculatum.** Hood destitute of a mucro or appendage, sometimes itself obsolete. — In mountains near Morales, San Luis Potosi, *Schaffner*, no. 271 in part; base of Iron Mountain, Durango, *Dr. E. Palmer*, no. 926 (coll. of 1896); Guanajuato, *Prof. A. Dugès, Pringle*, no. 5309; Federal District, *Pringle*, no. 7978 (form approaching *M. hispidum*, HBK).

+ + Ligules conspicuous, usually much exceeding the fructiferous bracts: peduncles long and slender.

++ Leaves (at least in part) pinnatifid; segments rather broad.

10. M. AMERICANUM, L. Spec. ii. 921 (1753); Rel. Houst. 9, t. 21; DC. Prodr. v. 518. — Vera Cruz, Mexico, *Houston*. With this clearly figured plant from Vera Cruz I have been unable to match any specimens from Southeastern Mexico. However, the following specimens from the western coast probably belong here: Manzanillo, *Xantus*, and Colima, *Palmer*, no. 136 (coll. of 1897), and no. 1172 (coll. of 1891).

++ ++ Leaves, at least in part, deeply cleft, segments narrow, linear.

= Outer bracts of the involucre pointless, surrounded by a thin yellow somewhat hyaline border.

11. M. LINEARILOBUM, DC. Prodr. v. 518 (1836). *M. sericeum*, Benth. in Oerst. Vidensk. Meddel. 1852, p. 86, not Lag. — A well-marked species represented by the following specimens: Oaxaca, *Nelson*, nos. 2809, 2339 (pathological); Chiapas, *Nelson*, no. 2949; Guerrero, hills near Iguala, *Pringle*, no. 9162; Nicaragua, *Oersted;* Sinaloa, *Rose*, no. 3183.

= = Outer bracts of the involucre not membraneous-margined or colored, herbaceous to the acuminate apex.

12. M. **longipes.** *M. sericeum*, var. *longipes*, Gray, Proc. Am. Acad. xxii. 423 (1887). — Erect, 4 to 5 dm. high, widely branched: upper and

lower leaves entire, lance-linear, acute at both ends, 4 to 5.5 cm. long, 4 to 5 mm. broad, the middle cauline leaves deeply and pinnately 3-cleft into linear acute segments, finely pubescent above, flocculent-sericeous beneath: peduncles filiform, springing from the forks, 2 to 5 cm. long: heads 1.2 to 1.4 cm. broad (including the rather numerous well-exserted narrow bright yellow ligules): fruit tuberculate, the hood well developed and passing gradually and without intermediate toothing into a long slender spirally coiled appendage. — Jalisco, Mexico, on dry hillsides near Tequila, *Dr. Edward Palmer*, no. 391 (coll. of 1886), *C. G. Pringle*, no. 4598. Type in herb. Gray. This plant although in habit identical with *M. heterophyllum*, Lag., is strictly herbaceous and annual. This fact, together with the hooded and appendaged fruit, seems to warrant its separation. It is certainly distinct from *M. sericeum*, Lag.

++ ++ ++ Leaves undivided.

13. M. Kunthianum, DC. Prodr. v. 519 (1836). *M. sericeum*, HBK. Nov. Gen. & Spec. iv. 272, t. 398 (1820), not Lag. — Of this species I have seen only a single and imperfect specimen in the De Candollean Herbarium. The leaves are linear, or nearly so, and entire; the fruit is provided with a well-developed hood but no appendage. This species also exhibits a suspicious resemblance to *M. heterophyllum*, Lag., and it may represent Lagasca's var. *β*.

14. M. diffusum, Cass. Dict. lix. 238 (1829). *M. manillense*, Less. Linnaea, vi. 155 (1831). After examining authentic material of this species in the Prodromus herbarium I can confidently refer to it Dr. Palmer's nos. 3 and 281 from Acapulco, Mexico (coll. of 1895). The species has been hitherto recorded only from the Island of Luzon. As the genus as a whole is American, and as this species is now found to be also an American plant, its occurrence in the Philippines may very likely be due to introduction. At all events it seems from the distribution of the other species more likely that this plant has been carried from Mexico to the Philippines, than the reverse.

Var. lanceolatum. *M. lanceolatum*, DC. Prodr. v. 519 (1836). — Fruit with a short hood but no appendage; otherwise closely like the typical form. — Collected by Nee, but the locality unknown. Nee visited both Acapulco, Mexico, and the Philippine Islands.

§ 2. Zarabellia, DC. Fructiferous bracts not exceeding the inclosed achenes, nor developed into a cup, hood, or appendage at the summit. — Prodr. v. 519 (1836). *Zarabellia*, Cass. Dict. lix. 240.

* Peduncles long and slender: ligules well exserted, conspicuous.

+ Leaves sericeous beneath.

++ Leaves of diverse forms, partly entire, partly cleft: Mexican.

= Peduncles long: rays conspicuously exserted: sterile flowers numerous: pales yellow-tipped.

15. M. HETEROPHYLLUM, Lag. Gen. et Spec. Nov. 33 (1816); DC. l. c. — Tantoyuca, Huasteca, *Berlandier*, nos. 741, 2161, *Ervendberg*, no. 80; between San Luis Potosi and Tampico, *Palmer*, no. 1103 (coll. of 1879).

= = Peduncles short or none: rays 3 to 4, minute: sterile flowers 1 to 3: pales purple-tipped.

16. **M. Pringlei.** Root perpendicular, long, with fibrous branches, probably annual; stem copiously branched from the base; the branches terete, purple, hirsute: leaves chiefly undivided, narrowly elliptic-lanceolate, 2 to 3 cm. long, 3 to 6 mm. broad, acutish, finely subappressed-pubescent above, snowy-sericeous beneath: lower heads short-peduncled from the forks, the upper subsessile, lateral and terminal, all small and few-flowered; outer bracts of the involucre 5, lance-linear and acute or somewhat spatulate, 3.5 mm. long, so narrow as to disclose the young fruit at an early stage in its development: ray-flowers 3 to 4; ligules very small, oval or sub-orbicular, entire or slightly 2-toothed: pales purple tipped; disk-flowers 1 to 3, mostly reduced to a clavate rudiment: fruit of the ray-flowers obovoid, strongly tuberculate, destitute of hood, cup, or appendage. — Collected by C. G. Pringle, at Las Sedas, Oaxaca, altitude 1,850 m., 15 September, 1894, no. 5722. Type in herb. Gray.

++ ++ Leaves all undivided, linear: South American.

17. M. ANGUSTIFOLIUM, DC. l. c. (1836). — Peru, *Haenke*.

+ + Leaves not sericeous beneath.

++ Slightly lignescent perennial: Lower California.

18. M. SINUATUM, Brandegee, Proc. Calif. Acad. Sci. ser. 2, iii. 144 (1891). — San José del Cabo, *Brandegee*, no. 302.

++ ++ Mexican and S. American species: annuals except *M. montanum*.

= Leaves cordate- or auriculate-clasping at the base.

19. **M. Rosei.** Erect annual, 3 to 4 dm. high; stem purplish, copiously branched almost from the base, covered with short white retrorse hairs: leaves oblong-lanceolate, attenuate, sinuately toothed, slightly narrowed to auriculate-clasping somewhat connate bases, sparsely pubescent upon both surfaces, scabrous on the margin, scarcely paler beneath, the larger about 7 cm. long, 2.5 cm. broad: peduncles in the forks of the stem, 7 cm. long, filiform, retrorsely pubescent; outer involucre 5-parted, the divisions broadly ovate or suborbicular, rounded or barely pointed at the apex, pubescent upon the back: ray-flowers 8 to 10, ligules oblong,

golden yellow, 2-toothed at the tip, about 4 mm. long; fructiferous bracts (without hood or appendage) marked with 3 rows of tubercles upon each lateral surface. — Collected by Dr. J. N. Rose between Rosario and Concepcion, Sinaloa, no. 3271. Type in herb. U. S. Nat. Museum.

Var. **subintegrum**. Leaves clasping at the base but their margins unlobed, obsoletely crenate-serrate. — Collected by Dr. J. N. Rose at Rosario, Sinaloa, 7 July, 1897, no. 1568.

20. **M. mimulifolium.** Dichotomously branched herb; stems purplish-streaked, loosely villous and finely pubescent along a longitudinal line: leaves lanceolate, acuminate, entire or obsoletely serrulate, 5 to 7 cm. long, 1.2 to 2 cm. broad, appressed-pubescent upon both surfaces, somewhat narrowed to an auriculate amplexicaul base: peduncles in the forks of the stem, 4 cm. long, filiform, covered with a fine spreading pubescence: outer involucre 5-parted; segments ovate-lanceolate, acute, somewhat accrescent, appressed-villous: ligules about 8, short-oblong, 2–3-toothed: fruit short, broad, somewhat quadrate, without hood or appendage, compressed, thin, depressed upon the lateral faces, finely tuberculate dorsally. — Collected by E. W. Nelson in the vicinity of Totontopec, Oaxaca, altitude 1700 to 2150 m., 15 July, 1894, no. 740. Type in herb. U. S. Nat. Museum. The foliage recalls that of *Mimulus ringens*.

= = Leaves neither cordate nor auriculate-clasping (except obscurely so in *M. gracile*).

a. Divisions of the outer involucre 3, ovate to ovate-lanceolate, acute or acuminate.

21. M. PANICULATUM, Gardn. in Hook. Lond. Jour. Bot. vii. 287 (1848). — Eastern and Central Brazil.

22. M. GRACILE, Less. Leaves rhombic, unlobed or panduriform, more or less narrowed to an obscurely auriculate or at least obtuse base. — Linnaea, vi. 407 (1831). — Papantla, *Schiede & Deppe;* Tantoyuca, Huasteca, *Ervendberg*, no. 92; Julapa, *C. L. Smith*, no. 1605.

23. M. OBLONGIFOLIUM, DC. Leaves oblong to oblong-lanceolate, acute to attenuate at the base, never lobed. — Prodr. v. 519 (1836). — Vera Cruz, near Orizaba, *Botteri*, no. 809, *Seaton*, no. 461, Cordova, *Bourgeau*, no. 1628, near Tantoyuca, *Berlandier*, no. 733; Oaxaca, at San Felipe, *Conzatti & González*, no. 560; Michoacan, *Pringle*, no. 4322; Morelos, *Pringle*, no. 7321; Costa Rica, *Pittier*, no. 6963.

b. Divisions of the outer involucre 5, obliquely acuminate.

24. M. MICROCEPHALUM, Less. Linnaea, ix. 268 (1834). — This species is known to me only from Lessing's characterization and from an excellent tracing, prepared from the type at Berlin by Mr. J. M. Green-

man. It is evidently close to *M. paludosum* in habit and foliage, differing chiefly, as Lessing himself notes, in its obliquely acuminate instead of rounded or obtuse involucral bracts.

c. Divisions of the outer involucre obovate, rounded or obtuse.

1. Decumbent perennial with elliptical discolorous leaves and pale yellow rays (often tinged with purple).

25. M. MONTANUM, Benth. Pl. Hartw. 64 (1840). *M. Liebmannii*, Sch. Bip. in Klatt, Leopoldina, xxiii. 89 (1887). — Oaxaca, *Graham*, *Pringle*, no. 4666; Chiapas, *Ghiesbreght*, nos. 174, 564; San Luis Potosi, *Pringle*, no. 3818; Cumbre de Estepà and Yavesia, *Liebmann*, no. 232.

2. Erect annuals.

26. M. TENELLUM, Hook. & Arn. Bot. Beech. 299 (1840). — Acapulco, *Sinclair*.

27. M. CUPULATUM, Gray, Proc. Am. Acad. viii. 291 (1870). — Sonora, *Palmer*, no. 20; Mazatlan, *W. G. Wright*, no. 1213; Alamos, *Palmer*, no. 726 (coll. of 1890). This species may possibly prove identical with the preceding. Both are distinguished from the following by their narrow lance-linear or oblong-linear leaves.

28. M. PALUDOSUM, HBK. Nov. Gen. & Spec. iv. 273 (1820). *M. divaricatum*, DC. Prodr. v. 520 (1836). *M. pumilum*, Benth. Pl. Hartw. 64 (1840), described from starved specimens. *M. copiosum* and *M. panamense*, Klatt in Engl. Jahrb. viii. 41, 42 (1887), founded upon trifling foliar variations without accompanying floral distinctions. *Dysodium divaricatum*, Rich. in Pers. Syn. ii. 489 (1807). *D. radiatum*, Desf. Cat. Hort. Paris, 1829, p. 182. *Alcina ovalifolia*, Lag. "Elench. Hort. Madr. 1805," Gen. et Spec. Nov. 32 (1816). *A. ovatifolia*, Jacq. f. Eclog. i. 115, t. 78 (1815?). *A. minor*, Cass. Dict. lix. 243. *Wedelia ovatifolia*, Willd. Suppl. 61 (1813). *W. minor*, Hornem. Hort. Hafn. 855 (1813). — A common weed throughout Mexico, Central America, and also occurring in the West Indies. Highly variable in leaf contour, length of ligules, etc., thus passing into many very diverse yet seemingly unstable forms.

* * Rays short, inconspicuous, exceeded by the involucre: peduncles short or none.

+- Leaves ovate-lanceolate, rounded at the subsessile base: Panama to Brazil.

29. M. CAMPHORATUM [Benth. & Hook. f. Gen. ii. 349 (1873)], Baker in Mart. Fl. Bras. vi. pt. 3, 161 (1884). *M. digynum*, Benth. & Hook. f. l. c. acc. to Hook. f. & Jacks. Ind. Kew. ii. 188. *Unxia camphorata*, L. f. Suppl. 368 (1781). *U. digyna*, Steetz in Seem. Bot. Herald, 154, t. 30 (1852–1857). — Panama, *Seemann*, and Llanos de

Cumaral, Colombia, *André*, no. 1120, to British Guiana and tropical Brazil, where apparently common.

+ + Leaves narrowed to a petiole or an exauriculate base: stems solitary.

++ Leaves rhombic to elliptic-oblong, obscurely toothed, undivided.

30. M. FLACCIDUM, Benth. Vidensk. Meddel. 1852, 86. *M. tenellum*, var. *flaccidum*, Benth. Bot. Sulph. 115 (1844). — Nicaragua near Granada, *Oersted;* Costa Rica, San Francisco de Guadalupe, *Tonduz*, nos. 7187, 8498; Tepic, Mexico, *Hinds*, *Palmer*, no. 1814 (starved specimens).

++ ++ Leaves narrow, linear-oblong and unlobed or deeply cleft into narrowly oblong segments.

31. M. HISPIDUM, HBK. Nov. Gen. & Spec. iv. 273, t. 399 (1820). *M. coronopifolium*, Sch. Bip. in Hemsl. Biol. Cent.-Am. Bot. ii. 145 (1881), without character. — Arizona, Apache Pass, and near Ft. Huachuca, *Lemmon*, nos. 331, 2795, Santa Rita Mountains, *Pringle ;* Sonora, *Wright*, no. 1205; Chihuahua, *Pringle*, no. 297; Durango, *Palmer*, no. 486 (coll. of 1896); San Luis Potosi, *Parry* & *Palmer*, no. 444½; Jalisco, *Palmer*, no. 260 (coll. of 1886), in part; Tacubaya, *Bilimek*, no. 593, *Schaffner*, no. 195. — Except in the nature of the pubescence this species closely simulates *M. sericeum*, Lag.

+ + + Leaves obovate, narrowed to an exauriculate base: stems several from the very base.

32. **M. arvense.** Prostrate spreading annual; root fibrous; stems several, 1 to 2 dm. long, more or less branched, purplish, covered all around with short weak white hairs: leaves obovate, entire or obsoletely crenate, rounded at the apex, 3-nerved above the acuminate and slightly connate base, bright green and glabrous or nearly so upon the upper surface, distinctly paler and hispidulous upon the nerves beneath, 1.2 to 2.5 cm. long, 1 to 1.6 cm. broad: heads very small, surrounded by small ovate to orbicular foliaceous bracts and borne close in the forks of the stem and also upon such short lateral cymes as to appear axillary; outer bracts of the involucre 2, ovate, distinct at the base, obtusely pointed: ray flowers 1 to 3, disk flowers about equally numerous: fruits semi-obovate, strongly compressed, reticulated upon the sides, more or less tuberculate dorsally. — Collected by C. G. Pringle in the Valley of Mexico, Federal District, 19 October, 1896, no. 7327 (type, in herb. Gray), and in fields near Toluca, 26 September, 1892, no. 5257, also at an earlier date by Schaffner in mountains near Santa Angela. Nearest *M. bibracteatum*, Wats., but differing markedly in the contour and cuneate base of the leaves as well as in its prostrate several-stemmed habit.

+ + + + Leaves rhombic to oblong, narrowed to a sessile auriculate base.

++ Leaves oblong, relatively narrow.

= Outer involucral bracts 2, not accrescent, or scarcely so.

33. M. BIBRACTEATUM, Watson, Proc. Am. Acad. xxvi. 140 (1891). Fields, Del Rio, State of Mexico, *Pringle*, no. 3230.

= = Outer bracts 4 to 5, obtuse, united at the base into a cup.

34. M. GLABRUM, Watson. Proc. Am. Acad. xxvi. 139 (1891). — Guanajuato in valley near Irapuato, *Pringle*, no. 2821, and Jalisco near La Barca, *Pringle*, no. 3863.

++ ++ Leaves broad, mostly obovate or rhombic: outer involucral bracts 5, conspicuously accrescent.

= Outer bracts of the involucre lance-oblong, acute, distinct nearly or quite to the base.

35. M. LONGIFOLIUM, Cerv. acc. to Cav. Anal. Cien. Nat. vi. 303 (1803). *M. rhomboideum*, DC. Prodr. v. 520 (1836). — San Luis Potosi, *Parry & Palmer*, no. 444; Valley of Mexico, *Bourgeau*, no. 868, *Pringle*, no. 6455, *Harshberger*, no. 176.

= = Outer bracts of the involucre ovate, obtuse or obtusish, connate toward the base.

36. M. PERFOLIATUM, HBK. Nov. Gen. & Spec. iv. 274 (1820). — A common and well-marked weed throughout Mexico, also established in S. California at Los Angeles, *Parish Brothers.*

SYNONYMS AND DOUBTFUL OR EXCLUDED SPECIES.

M. achillaeoides, Hemsl. Biol. Cent.-Am. Bot. ii. 145 (1881) = *Villanova achillaeoides*, Less.

M. australe, Loefl. It. Hisp. 268 (1758) = *Acanthospermum brasilum*, Schrank, acc. to Hook. f. & Jacks. Ind. Kew. ii. 188.

M. Baranguillae, Spreng. Syst. iii. 619 (1826) [*M. Baranquillae*, DC. Prodr. v. 521] = *Sclerocarpus africanus*, Jacq., acc. to DC. Prodr. v. 521.

M. Berterianum, Spreng. l. c. An unrecognized and poorly described West Indian plant, very likely not of this genus.

M. brachyglossum, J. D. Smith, Bot. Gaz. xiii. 74 (1888) = *Jaegeria hirta*, Less.

M. copiosum, Klatt in Engl. Jahrb. viii. 41 (1887) = *M. paludosum*, HBK.

M. coronopifolium, Sch. Bip. in Hemsl. l. c. = *M. hispidum*, HBK.

M. digynum, Benth. & Hook. f. Gen. ii. 349 (1873), acc. to Hook. f. & Jacks. l. c. = *M. camphoratum*, Benth. & Hook. f.

M. divaricatum, DC. l. c. = *M. paludosum*, HBK.

M. Dombeyanum, DC. l. c. 521, is a still doubtful species from Peru.

M. Hildalgoa, DC. l. c. = *Hildalgoa ternata*, Llav. & Lex.

M. hirsutum, Benth. & Hook. f. l. c. acc. to Hook. f. & Jacks. l. c. = *M. camphoratum*, Benth. & Hook. f.

M. humile, Sw. Prodr. Veg. Ind. Occ. 114 (1788) = *Acanthospermum humile*, DC.

M. lanceolatum, DC. Prodr. v. 519 (1836) = *M. diffusum*, var. *lanceolatum*.

M. Liebmannii, Sch. Bip. in Klatt, Leopoldina, xxiii. 89 (1887) = *M. montanum*, Benth.

M. longifolium, Brouss. ex Willd. Enum. Hort. Berol. 934 (1809) = (?) *M. longifolium*, Cerv.

M. manillense, Less. Linnaea, vi. 155, t. 2 (1831) = *M. diffusum*, Cass.

M. ovatifolium, Reichenb. Ic. Exot. t. 42 (1827) = *M. paludosum*, HBK.

M. panamense, Klatt, l. c. 42 = *M. paludosum*, HBK.

M. pumilum, Benth. Pl. Hartw. 64 (1840) = starved *M. paludosum*, HBK.

M. ramosissimum, DC. Prodr. v. 518 (1836) = *M. cinereum*, var. *ramosissimum*, Gray.

M. rhomboideum, DC. l. c. 520 (1836) = *M. longifolium*, Cerv.

M. ruderale, Sw. Fl. Ind. Occ. iii. 1372 (1806) = *Eleutheranthera ovata*, Poit., acc. to Hook. f. & Jacks. l. c.

M. sericeum, Benth. in Oerst. Vidensk. Meddel. 1852, p. 86, not Lag. = *M. linearilobum*, DC.

M. sericeum, var. *brevipes*, Gray, Proc. Am. Acad. xxii. 423 (1887) = typical *M. sericeum*, Lag.

M. sericeum, var. *longipes*, Gray, Proc. Am. Acad. xxii. 423 (1887) = *M. longipes*, Robinson.

M. ternatum, DC. acc. to Hook. f. & Jacks. Ind. Kew. ii. 188, = *Hidalgoa ternata*, Llav. & Lex.

It must be frankly confessed that among the species here kept up the following are to the writer still doubtful: —

M. americanum, L., which, although the type of the genus, cannot be matched by any specimen from near the original station.

M. microcephalum, Less. Not as yet satisfactorily represented in the herbaria examined.

M. paludicola, Taub., the description of which suggests a *Sclerocarpus*.

M. paniculatum, Gardn., which from description is not clearly separable from *M. oblongifolium*, DC.

II. — SYNOPSIS OF THE GENUS NOCCA.

NOCCA, Cav. Icon. iii. 12, t. 224 (1795); Pers. Syn. ii. 498 (1807); La Llave & Lex. Nov. Veg. i. 31 (1824); Spach, Hist. x. 40 (1841). *Noccaea*, Willd. Spec. iii. 2393 (1804); Jacq. Frag. 58, t. 85 (1805); Spreng. Anleit. ii. 548 (1818); Less. Linnaea, vi. 695 (1831), & Syn. 151 (1832); not Moench. *Lagasca*, Cav. Ann. Cien. Nat. vi. 331 (1803). *Lagascea*, Willd. Enum. Hort. Berol. 941 (1809); Spreng. l. c. 549 (1818); HBK. Nov. Gen. & Spec. iv. 24 (1820); DC. Prodr. v. 91 (1836); Benth. & Hook. f. Gen. Pl. ii. 342; Hoffmann in Engl. & Prantl, Nat. Pflanzenf. iv. Ab. 5, 212. — Heads 1- to rarely 2-flowered, aggregated in dense campanulate or subglobose capitate glomerules; these subtended by ovate to linear more or less specialized herbaceous bracts; proper involucre calyx-like, tubular, gamophyllous, 5-toothed. Flowers alike, perfect, fertile. Corolla with narrow proper tube, enlarged cylindric throat, and 5-toothed limb, yellow to white or reddish purple, well exserted from the surrounding involucre. Style-branches long, attenuate; achenes columnar or attenuate toward the base; pappus of 2 to several short scales or rudimentary. — Annual herbs or more often shrubs, probably all natives of tropical America, a single annual species now widely distributed in the tropics. Leaves chiefly opposite. The name *Nocca* (given by Cavanilles in 1795 in honor of *Dominico Nocca*, professor of botany at Padua) is clearly the one to be employed for this genus by those who wish to apply consistently the generally conservative Berlin Rules. From the definite characterization and excellent figure given by Cavanilles there can be no doubt as to the identity of his genus *Nocca*, and the fact that the name was taken up in the same sense within fifty years by Persoon, Jacquin, La Llave, and Sweet, should establish its validity. The form *Noccaea*, adopted by various botanists from Cassini to Kuntze, may be regarded as a different spelling of the same name. Although substantive in form it has no advantage over *Nocca* commensurate with the indefiniteness which succeeds any modification of a name as originally published, and it is preferable therefore to take the name in its earliest form. While always reluctant to change any current generic name like *Lagascea*, I hesitate the less in this instance from the fact that this genus has attained no importance in horticulture or pharmacy, and its nomenclature has accordingly little or no significance outside technical systematic botany.

* Involucres 2-flowered.

1. N. BIFLORA, O. Kuntze, Rev. Gen. i. 354 (1891), as *Noccaea. Lagascea biflora*, Hemsl. Diag. Pl. Nov. 33 (1879), & Biol. Cent.-Am. Bot. ii. 139, t. 44 (1881). — Mexico, without locality, *Parkinson*, Salina Cruz, *C. C. Deam.*

* * Involucres 1-flowered.

+ Shrubs or perennial herbs: Mexican.

++ Flowers large: glomerules sessile or scarcely peduncled, even in age more or less campanulate, the subtending bracts ovate to lanceolate, large and conspicuous: central and southern Mexico.

= Leaves cordate-clasping at the sessile base.

2. N. HELIANTHIFOLIA, Cass. Stem pilose: leaves scabrous above, scabro-hirtellous beneath. — Dict. Sci. Nat. xxv. 104 (1822), as *Noccaea. Lagascea helianthifolia*, HBK. Nov. Gen. & Spec. iv. 25 (1820). *L. macrophylla*, Zucc. acc. to Steud. Nomen. ed. 2, ii. 4 (1841). *Noccaea macrophylla*, Zucc. acc. to DC. Prodr. v. 92 (1836). Acapulco, Mexico, *Humboldt* & *Bonpland;* Jalisco, Rio Blanco, *Palmer*, no. 664 (coll. of 1886); Guadalajara, *Pringle*, no. 1824, in part.

Var. **levior.** Stem pulverulent-puberulent, destitute of the long spreading pilosity characteristic of the typical form: leaves scabrous above, scabrous-hirtellous beneath. — Colima, Mexico, *Dr. Edw. Palmer*, no. 1148 (coll. of 1891); Zopelote, Tepic, altitude 615 to 924 m., *Lamb*, no. 561.

Var. **suaveolens.** Stem pilose; leaves soft-pubescent beneath. — *Lagascea suaveolens*, HBK. l. c. (1820). *Noccaea suaveolens*, Cass. l. c. 105 (1822). *Nocca latifolia*, Cerv. in La Llav. & Lex. Nov. Veg. i. 31 (1824). *Lagascea latifolia*, DC. Prodr. v. 92 (1836). — Tamaulipas, Santa Barbara, *Berlandier*, nos. 753, 2173; Guanajuato, *Dugès* (a form resembling the type); Oaxaca, *Nelson*, no. 1804, *L. C. Smith*, no. 964; *Conzatti* & *González*, no. 558, *Holway*, no. 3724; Puebla, *Conzatti*, no. 861; Vera Cruz, Mirador, *Liebmann*, no. 111; Orizaba, *Schaffner*, *Bourgeau*, no. 3342, *Botteri*, no. 499, *Gray*, Tantoyuca, *Ervendberg*, no. 317; Chiapas, *Ghiesbreght*, nos. 146, 571 (form with leaves exceptionally pubescent almost lanate beneath); Guatemala, J. D. Smith's nos. 2410, 4227.

= = Leaves short-petioled, ovate, 2 or 3 times as long as broad: flowers red or purple.

a. Indumentum of the stem spreading, dense, uniform in length, partially glandular: leaves elliptic, obtusish, remotely denticulate.

3. N. N. SP. [?]. Branches lignescent, covered throughout by a fine dense spreading pubescence, a part of the hairs glandular, others of

equal length without glandular tip, not rubescent: leaves elliptical-obtusish or very shortly acuminate, grayish-pubescent beneath, somewhat scabrous upon both surfaces, shortly but manifestly petiolate, the upper leaves much reduced, oblanceolate, acuminate, remotely denticulate, much shorter than the rather elongated internodes; secondary nerves 2 or 3, originating some distance above the base: bracts linear, acute, exceeding the flowers. — *Lagascea Moçinniana*, DC. Prodr. v. 92 (1836) as to pl. of Haenke not of Mociño. — Mexico without locality, *Haenke*, in herb. De Candolle. For an excellent sketch of this plant and information concerning it I am indebted to the kindness of Mr. Robert Buser.

b. Indumentum unknown: leaves ovate, acute, green upon both surfaces, finely serrulate with approximate purple-glandular teeth (about 10 to the centimeter).

4. N. Moçinniana, O. Kuntze, l. c. (1891), as *Noccaea Moçiniana. Lagascea Moçinniana*, DC. Prodr. v. 92 (1836) as to pl. of Mociño. — Mexico without locality, *Mociño*.

c. Indumentum of the stem widely spreading, composite, consisting of a dense short gray subglandular puberulence and a long white horizontally spreading villosity: leaves ovate, serrate, the margins neither purple nor glandular; both surfaces grayish-pubescent.

5. **N. Pringlei.** Stems slightly lignescent, 1 to 2 m. high, brown, in dried state striate, covered with a fine spreading gray puberulence and long spreading white villosity: leaves ovate, somewhat rigid, 5.5 to 6.5 cm. long, 3 to 4 cm. broad, serrate with about 2 teeth to the centimeter, 3-nerved from much above the base and pinnately veined, gray-tomentose upon both surfaces, especially so beneath, obtuse or acutish at the apex, rounded at the base; petiole 3 to 4 mm. long: branches of the inflorescence rigid, divergent, with long internodes and spatulate bracts; glomerules rather loose, not many-flowered: involucres 1-flowered, cylindrical, upwardly canescent-villous, 1 cm. long, cleft nearly to the middle into 5 erect very unequal teeth: corolla 1.2 cm. long, purple, covered on the outside with a fine gray tomentum; the tube very short, slender; the throat cylindrical, 4 to 5 mm. in length; teeth 5, ovate, scarcely acute: mature achene not seen. — Collected by C. G. Pringle on limestone ledges above Iguala, Guerrero, Mexico, 10 October, 1900, no. 8400. Type in herb. Gray.

d. Indumentum of the stem fine, appressed: leaves elliptic-ovate, finely or more coarsely serrate, but not noticeably purple-glandular on the margin.

1. Leaves green, lucid, and scabrous-pubescent upon both surfaces.

6. N. rigida, Cav. Ic. iii. 12, t. 224 (1795); Sweet, Brit. Fl. Gard. ser. 2, t. 26. *Noccaea rubra*, Cass. l. c. 104 (1822). *Lagascea rubra*, HBK. l. c. 24, t. 311 (1820). — Mexico, Cordillera of Guihilaque,

Berlandier, no. 1018; State of Mexico, *Bourgeau*, no. 1235, *Schaffner*, no. 293, *Pringle*, nos. 3500, 3896, 9098; Cuernavaca, *Bourgeau* no. 1205.

2. Leaves green above, niveous-sericeous beneath.

7. N. Heteropappus, O. Kuntze, l. c. (1891) as *Noccaea*. *Lagascea Heteropappus*, Hemsl. Diag. Pl. Nov. 33 (1879). — Mexico, *Parkinson*, without locality; hillsides near Morelia, Michoacan, *Pringle*, no. 4541.

e. Indumentum of the stem spreading, compound, the short glandular hairs much exceeded by a long non-glandular villosity; leaves ovate-oblong, attenuate, dull and gray-pubescent upon both surfaces, even the upper ones exceeding the internodes.

8. **N. tomentosa.** *Lagascea tomentosa*, Rob. & Greenm. Proc. Am. Acad. xxxii. 43 (1896). — Guerrero, Mexico, between Ayusinapa and Petatlan, *E. W. Nelson*, no. 2121.

= = = Leaves oblong-oblanceolate, 4 to 5 times as long as broad, narrowed at the base to a distinct petiole.

9. N. angustifolia, O. Kuntze, l. c. (1891) as *Noccaea*. *Lagascea angustifolia*, DC. Prodr. v. 92 (1836). — N. W. Mexico, *Seemann*; Durango, *Palmer*, no. 853 (1896); Jalisco, *Palmer*, no. 643 (1886), *Pringle*, no. 1784.

↔ ↔ Glomerules slender-peduncled, usually raised much above the foliar leaves, at length subglobose, the subtending bracts mostly small and narrow.

= Teeth of the gamophyllous involucre relatively long and narrow, lance-linear to subulate.

a. Involucres soft-villous.

10. N. decipiens, O. Kuntze, l. c. (1891) as *Noccaea*. *Lagascea decipiens*, Hemsl. Diag. Pl. Nov. 33 (1879), & Biol. Cent.-Am. Bot. ii. 140, t. 44, f. 1–4 (1881). — North Mexico in the Sierra Madre, *Seemann*, no. 2056; Southwestern Chihuahua, *Palmer*, no. 145 (coll. of 1885); Sonora, at Guaymas, *Palmer*, no. 256 (coll. of 1887), Alamos, *Palmer*, no. 401 (1890), La Tinaya, *Hartmann*, no. 249.

b. Involucre hirsute.

11. **N. glandulosa.** *Lagascea glandulosa*, Fernald, Bot. Gaz. xx. 534 (1895). — W. Mexico, head of Mazatlan River, *W. G. Wright*, no. 1305; Rosario, Sinaloa, *Lamb*, no. 483.

= = Teeth of the involucre very short (1 to 1½ mm. in length), ovate to deltoid-lanceolate.

a. Stem and floral branches pubescent to tomentulose.

12. **N. Liebmannii.** *Lagascea Liebmannii*, Sch. Bip. in Klatt, Leopoldina, xx. 91 (1884). — Leaves soft-pubescent beneath: involucre

finely villous, 6 to 7 mm. long: corolla 7 mm. long, puberulent, the teeth ovate. — Pochutla, Oaxaca, *Liebmann*, no. 250 (type in herb. Bot. Gard. Copenhagen; fragment and good sketch in herb. Gray).

b. Stem and floral branches glabrous.

13. **N. Palmeri.** Slender-stemmed shrub, with terete divaricate glabrous branches; internodes long, in dried state finely ribbed: leaves ovate, acute, scabrous both above and beneath with enlarged and indurated bases of trichomes (in the manner of many *Borraginaceae*), nearly or quite entire, 1.5 to 2.5 cm. long, abruptly narrowed at the base to a very short petiole: floral branches opposite; peduncles slender, 2 to 4 cm. long; glomerules 2.5 cm. in diameter, subglobose, about 25-headed; subtending bracts ovate-oblong to narrowly oblong, 6 to 8 mm. in length, their pubescence similar to that of the leaves; involucres terete, 10-nerved, 1 cm. long, sparingly villous; segments deltoid-lanceolate, minutely ciliated: corolla 1 cm. long, essentially glabrous; its teeth elliptic-oblong, 3 mm. in length, 2-nerved: pappus a finely fringed campanulate cup. — Collected by Dr. Edward Palmer, at Colima, Mexico, 27 to 28 February, 1891, no. 1320.

+ + Annual: tropics of both hemispheres.

14. N. MOLLIS, Jacq. Frag. 58, t. 85 (1809). *Lagasca mollis*, Cav. Ann. Cien. Nat. vi. 333, t. 44 (1803). *Noccaea mollis*, Cass. l. c. 103 (1822). *Lagascea Kunthiana campestris*, Gard. in Hook. Lond. Journ. Bot. v. 238 (1846). *Lagasca parvifolia*, Klatt, Ann. k. k. Nat. Hofmus. Wien, ix. 360 (1894). — Western and southern Mexico, tropical South America, West Indies, also Bengal, etc.

III. — NEW SPECIES AND NEWLY NOTED SYNONYMY AMONG THE SPERMATOPHYTES OF MEXICO AND CENTRAL AMERICA.

Dioscorea platycolpota, E. B. Uline in litt. "Glabrous throughout; stem stout, dextrorsely twisted; leaves membranaceous, orbicular-cordate, 9 to 11-nerved; ♂ racemes short, solitary, densely flower-bearing nearly to the base; flowers pedicellate, disposed in 3 to 5-flowered cymules, which in turn are closely arranged on the pendant rachis; perianth greenish yellow, campanulate, equalling or surpassing the slender pedicel; stamens three, rising divaricately from the somewhat fleshy receptacle, a little shorter than the ovate segments of the perianth; anthers extrorse. Pistillate spikes short, solitary; perianth very shortly stipitate; style

column slender, its slender, divaricate branches bifurcate at the apex; capsules small and crowded, obovate, leathery in texture; seed small, corrugated, with peripheral wing. — Collected by C. G. Pringle on limestone mountains near Iguala, State of Guerrerô, Mexico, altitude 1,230 m., 15 September, 1900, no. 9224. This plant exhibits close affinities for *D. Pringlei*, Rob., the essential floral characters being identical; but the striking difference displayed in its much larger and densely crowded flowers serves to give it an entirely distinct aspect, and seems to justify a specific description. Leaves 8 to 9 cm. in diameter. Racemes 12 cm. long, with rather stout rachis. Perianth 5 mm. wide; segments 4 mm. long. Capsules 7 to 8 mm. wide."

Calochortus Pringlei. Bulb ovoid, 3.5 cm. long, covered by more or less thickened somewhat reticulated fibres, and surmounted by a cylindrical mass of long linear fuscous scales, from the midst of which rises the stem; this 4 dm. high, terete, glabrous, simple or branched, 3–5-leaved: leaves flat, linear, attenuate, the basal 3 dm. long, the cauline gradually shorter; bracts of the spathe 2, opposite, subequal, 2 to 3 cm. long, lanceolate, acuminate; pedicels glabrous, 2 to 7 cm. long; flowers 3 cm. in diameter, dark purple or almost black; sepals narrowly obovate, bluntly pointed or retuse, glabrous except at a small roundish area a little below the middle on the inner surface: petals broadly obovate, cuneate, 1.4 cm. long, two-thirds as broad, obtusely pointed, externally glabrous, internally covered on all parts except the narrowed base by rather coarse violet or yellow hairs: filaments 5 lines long, glabrous; anthers 3.5 lines long, apiculate: ovary glabrous; capsule acute at each end, 2.5 cm. long, 8 mm. in diameter. — Collected by C. G. Pringle in thin soil of the top of knobs of the Sierra de Tepoxtlan, State of Morelos, Mexico, altitude 2,300 m., 15 September, 1900, no. 8435. Type in herb. Gray. Evidently related to *C. flavus*, Schultes, f. but differing in its dark colored flowers, short and broad fruit, etc.

MIMOSA ACANTHOCARPA, Benth., var. **desmanthocarpa.** Habit, foliage, and thorns of the typical form: pods unarmed, the valves minutely fulvous-tomentose. — Collected by E. W. Nelson between San Cristobal and Teopisca, Chiapas, Mexico, altitude 2,060 to 2,620 m., 4 December, 1895, no. 3428. Type in herb. U. S. Nat. Museum; fragment in herb. Gray.

Mimosa eurycarpoides. Branches glabrous, soft-woody, with rather large pith, terete or subangular, armed by a few small scattered spines: leaves large, (including the petiole) 1.2 to 2 dm. long; pinnae 7 to 12 pairs, 3.5 to 5 cm. long, puberulent upon the rachis; leaflets 20

to 30 pairs linear-oblong, 5 to 8 mm. long, 1.6 mm. wide, acutish, oblique at the base, finely appressed-pubescent upon both sides: flowers capitate, heads globose, 1.3 cm. in diameter; peduncles filiform, 1.5 cm. long, borne by twos and threes in the axils of the upper leaves: calyx turbinate-campanulate, scarious, slightly cuspidate-toothed, 0.8 mm. long: corolla 2.3 mm. long, glabrous, not conspicuously ribbed: stamens 8 or 10: pod 4.5 cm. long, 1.2 cm. broad, unarmed, glabrous, dark colored, oblanceolate, acute, thickish; valves not segmented. — Collected by Dr. J. N. Rose in the foothills of the Sierra Madre, near Colomas, State of Sinaloa, Mexico, 21 July, 1897, no. 1805. Type in herb. U. S. Nat. Museum; fragment in herb. Gray. To this species I should refer also Dr. Rose's no. 3157, collected on a road between Acaponeta and Rosario. While it is more copiously armed it shares all important characteristics with the plant from Colomas. The species is readily distinguished by its smooth unjointed fruit and axillary inflorescence.

Mimosa ionema. Shrub or small tree 3 to 5 m. high; branches unarmed, terete or nearly so, puberulent; branchlets green, angled and costate, tomentulose: stipules filiform, 8 mm. long, tomentulose under a lens; petioles angled, straight, puberulent-tomentulose, 4 to 6 cm. long, equalled by the foliar rachis; pinnae 4 to 6 subremote pairs, 5 cm. long, the lower ones commonly alternate; stipels 1 mm. long; leaflets about 15 pairs, oblong, obtuse, green and nearly or quite glabrous upon both surfaces, slightly paler beneath, oblique at the base, excentrically 1-nerved, pinnately veined, 1 cm. long, 3 to 4 mm. broad: flowers loosely spicate, spreading or somewhat deflexed; spikes fascicled by 3's and 4's in the axils of the upper leaves, ascending, 6 cm. long, on penduncles 2 to 3 cm. in length: corolla white or pale yellow, 2.5 mm. long, cleft to below the middle, without conspicuous nerves or ribs, glabrous; segments 4 to 5, lance-oblong, acutish: stamens 8 to 10; filaments violet-tinged: fruit (immature) narrowly oblong, acute at both ends, thin, glabrous, 5 cm. long, 7 mm. broad, about 8-seeded. — Collected by C. G. Pringle in the valley below Cuernavaca, Mexico, altitude 1,230 m., 17 October, 1900, no. 8377. Type in herb. Gray.

Mimosa Watsoni. Fruticose and probably scandent: stems subterete, tomentulose chiefly along six longitudinal lines, these bearing minute approximate subequal very short recurved spines: branchlets grayish-tomentose: petioles (including the rachis) 5 cm. long, rigid, angled, armed laterally and ventrally by 2 or 3 lines of recurved spines, tomentulose especially along the armed angles; pinnae 2 pairs; the lower bearing 1 or 2 pairs of leaflets, the upper with 2 or 3 pairs;

leaflets rhombic-ovate or obovate, lucid and finely pubescent above, tomentulose beneath, destitute of setae and ciliation, pinnately veined; the lateral 1.5 to 2.5 cm. long, subsymmetrical, the terminal twice as large, oblique and with excentric midnerve: globular heads (7 mm. in diameter) white, racemosely disposed on the long spreading unarmed grayish tomentose branches of a loose panicle; pedicels slender, 1 cm. long: corolla 4-parted to the middle, its lobes short-oblong, rounded at the apex: stamens 8: pods 5 cm. long, 7 to 10 mm. broad, glabrous and lucid upon the disarticulating valves but finely papillose under a strong lens, dark brown, unarmed except for a few scattered minute recurved spines upon the tomentulose replum; rectangular segments thin, broader than long. — Collected by the late Dr. Sereno Watson in the eastern portions of Vera Paz and Chiquimula, Guatemala, in 1885, nos. 323 in fruit and 185 in flower. Types in herb. Gray. This species of the subgenus *Habbasia* is closely related to the South American *M. Spruceana*, Benth. From this it differs, however, in the much less dense and less rufescent pubescence of the stem, more strongly armed petioles, less numerous leaflets of different venation and finally in its much smaller fruit, which is at full maturity less than half as broad as in the Brazilian plant.

Russelia Deamii. Stems becoming 1.6 m. long, 4-angled below, 6-angled toward the ends, copiously branched, glabrous except on the smaller branchlets, with slender ribs at the angles: leaves 1.5 to 2 cm. long, two thirds as wide, ovate, acute, incisely serrate except near the cuneate base, green, loosely pubescent and sparingly punctate above, slightly paler and strongly white-villous beneath especially about the larger nerves and near the base: cymes numerous, 3-flowered; peduncles slender, 4 mm. long, pubescent as are also the filiform slightly longer pedicels; bractlets linear: lobes of the villous calyx lance-acuminate from an ovate base: corolla scarlet, 1.6 to 2 cm. long, the nearly equal lobes suborbicular: fruit not seen. — Collected at Cuernavaca, Mexico, 7 July, 1900, by Charles C. Deam, no. 30. This species differs from *R. sarmentosa*, Jacq., in its villous more incisely toothed leaves and 6-angled branches, from *R. jaliscensis*, Rob., in the form of its calyx-lobes, from *R. polyedra*, Zucc., in its larger flowers and glabrous less strongly ribbed stems as well as in the form and sharp dentation of the leaves.

Russelia trachypleura. Stems 6-angled; angles prominent, rib-like, pale, roughened by small scattered callosities; areas between the ribs flat, green, glabrous or (especially near the nodes) somewhat hairy; branches usually 4-angled: leaves ternate on the stem, opposite on the

branches, elliptic-ovate, acute or acutish at each end, short-petioled, sharply serrate, green, resinous-dotted, and pubescent on the upper surface, slightly paler and pubescent upon the pinnately arranged veins beneath: flowers in short few-flowered axillary cymes: calyx-lobes ovate, caudate-acuminate, externally pubescent toward the sharp tip, 4 mm. long: corolla bright scarlet, 1.2 cm. long, with cylindrical tube and 4 short rounded subequal lobes, the upper one broader and emarginate. — Collected by C. G. Pringle on the Sierra de Tepoxtlan, State of Morelos, Mexico, altitude 2,300 m., 11 September, 1900, no. 9445. Readily distinguished from all the other species by the callosities on the rib-like angles of its stems.

Piqueria pyramidalis. Stem terete, 2 to 2.5 m. high, puberulent, green but maculate with elongated dark brown or purplish dots: leaves alternate (at least the upper ones), petiolate, broadly ovate, shallowly about 7-lobed, coarsely crenate, 3-nerved from the rounded to strongly cordate base, green and scabrous-puberulent above, paler and tomentulose beneath, the larger 1.7 dm. long and about as broad; petioles subterete, tomentulose: small and very numerous heads in pedicellate racemose glomerules; these forming a large leafy-bracted pyramidal panicle: involucral scales oblong, green, about 2-seriate, 2.5 to 3 mm. long, puberulent and covered with minute amber-colored particles upon the outer surface: corolla white, 3 mm. long, with short proper tube and relatively large throat, also bearing a few amber-colored particles: styles much exserted, clavate, purplish or brown; achenes dark-colored, glabrous, lucid, 2.5 mm. long. — Collected by C. G. Pringle in shade of cliffs on mountains above Iguala, altitude 1,230 m., 10 October, 1900, no. 8389. Type in herb. Gray. This species, although possessing all the technical characters of the genus, differs considerably in habit from the other Mexican species, being in fact nearer some of the South American.

Ageratum lucidum. Shrub with buff cortex and opposite spreading curved-ascending terete finely striate glandular-puberulent branches: leaves opposite, ovate, acutish, serrate from below the middle, thin, veiny, glabrous or early and completely glabrate upon both surfaces and lucid especially above, 4 cm. long, half as broad, ciliolate upon the margin, 3-nerved from somewhat above the abruptly acuminate shortly petiolate base, minutely white-dotted beneath and also covered with globular resinous or glandular atoms: corymbs long-peduncled (often irregularly compound), 2–6-headed and subtended by reduced opposite lance-oblong to linear sessile bracts; pedicels 1 to 2.4 cm. long, curved-ascending, 1-headed with or without 1 or more filiform bractlets; heads campanu-

late, 70–100-flowered, nearly 1 cm. in diameter; outer involucral scales linear-filiform, ciliated, the inner lance-oblong, acuminate, rigidulous, the subscarious margins erose: achenes black, 2 lines long, sharply angled, glabrous, very finely and transversely striate; pappus a shallow untoothed cup without awns. — Collected by C. G. Pringle, on mossy sides of conglomerate knobs of the Sierra de Tepoxtlan, near Cuernavaca, State of Morelos, Mexico, altitude 2,310 m., 31 October, 1900, no. 8362, and previously 15 March, 1899, no. 7851. Well marked. Type in herb. Gray.

Ageratum rhytidophyllum. Shrub with opposite terete dark red branches covered with a fine crisped cinereous puberulence: leaves opposite, subsessile, lance-oblong, 4 to 7 cm. long, 1.2 to 2 cm. broad, entire or obscurely serrate, revolute at the margin, acute at both ends, thickish, grayish green, scabrous-pubescent and strongly rugose above; veins much reticulated and prominulous beneath where covered by a dense spreading white pubescence; interstices covered by aureous particles: inflorescence of compound corymbs terminal upon the branches; bracts linear; heads rather small, 5 mm. in diameter, nodding on short glandular-puberulent pedicels, about 25-flowered; involucral scales unequal, pluriseriate, lance-linear, acute, pungent, green, striate, finely and sparingly pubescent; pales similar but narrower, rather rigid: corolla 3 mm. long, glabrous but covered with aureous particles; the proper tube greenish, about equalling the combined length of the whitish throat and lavender colored limb: achenes glabrous; pappus a short obscurely toothed cup. — Collected by C. G. Pringle on the Sierra de San Felipe, Oaxaca, Mexico, altitude 2,150 m., 5 October, 1894, no. 5675. Type in herb. Gray. Also secured in an immature state somewhat earlier (20 September, 1894) in the valley of Oaxaca by E. W. Nelson, no. 1446, and a little later (4 November, 1894) in the mountains of San Juan del Estado by Rev. L. C. Smith, no. 277.

Ageratum stachyofolium. Erect perennial with long tough filiform white roots; stem 5 to 6 dm. tall, terete, finely striate, purplish, densely covered with fine crisped white hairs: leaves elliptical, sessile or nearly so, mostly alternate, crenate, obtuse, pubescent upon both surfaces, 3-nerved, deep green above, paler green and veiny beneath, 3 cm. long, half as broad: corymbs terminal, simple, regular, 7–10-headed; bractlets filiform-spatulate; pedicels 2 to 2.5 cm. long, canescent-tomentulose; heads large for the genus, 1.2 cm. in diameter, about 100-flowered; scales of the involucre linear, acute, strongly striate, hirsute: achenes glabrous, sharply angled, dark brown, somewhat tapering toward

the base, 2 mm. long; pappus a short scarious untoothed cup without awns. — Collected by E. W. Nelson in the vicinity of La Parada, Oaxaca, altitude 2,310 to 2,620 m., 19 August, 1894, no. 991. Types in herb. Gray and herb. U. S. Nat. Museum.

Eupatorium anisopodum. Herbaceous perennial: stems terete, decumbent, flexuous, irregularly branched, puberulent especially near the nodes and under a strong lens, green or purplish tinged, 3 to 5 dm. high: leaves ovate or rhombic-ovate, opposite, 2 to 2.5 cm. long, 1.2 to 1.7 cm. broad, thickish, not punctate, crenate-serrate from the broadest portion to the acutish apex, covered above with fine short curved hairs, slightly paler beneath and appressed-pubescent upon the veins, 3–5-nerved, subcuneate at the base to a short petiole (5 mm. in length): bracts ovate-lanceolate, acute, 3 to 7 mm. long, the lower petiolate the upper sessile; heads small, 25–30-flowered, 5 to 7 mm. in diameter, not numerous, irregularly corymbose on pedicels of very unequal length; scales of the turbinate-campanulate involucre pluriseriate, very unequal, the outer short, ovate, acuminate, herbaceous, pubescent; the inner oblong, acute, pale, 2–3-nerved, ciliolate, sparingly pubescent or glabrous: corolla 2.2 mm. long, probably white, glabrous except at the limb where under a strong lens puberulent, the proper tube short, considerably exceeded by the subcylindric scarcely ampliate throat: achenes columnar, at length black, hispidulous on and between the five nerve-like angles, 1.5 mm. long; pappus-bristles 15 to 20, bright white, about equalling the corolla. — *E. pycnocephalum*, Coult. in J. Donnell Smith, Enum. Pl. Guat. ii. 94 (1891), not Less. — Collected by H. von Türckheim at Santa Rosa, Department Baja Vera Paz, Guatemala, altitude 1,540 m., April, 1887, no. 1177 of Mr. J. Donnell Smith's Guatemalan set. Type in herb. Gray. While possessing something the habit of *E. pycnocephalum*, Less., this plant is readily distinguished by its very different pluriseriate involucre.

EUPATORIUM ARALIAEFOLIUM, Less. Linnaea, vi. 403 (1831). Add syn. *E. heterolepis*, Robinson, Proc. Am. Acad. xxxv. 335 (1900).

EUPATORIUM BIGELOVII, Gray, Bot. Mex. Bound. 75 (1859). Add syn. *E. madrense*, Wats. Proc. Am. Acad. xxvi. 137 (1891).

EUPATORIUM CONSPICUUM, Kunth & Bouché, Ind. Sem. Hort. Berol. 1847, p. 13. Of this, *E. grandifolium*, Regel, Gartenflora, i. 102, t. 12 (1852), is certainly a synonym.

Eupatorium Coulteri. Stem slender, straight, terete, densely fuscous-puberulent: leaves opposite, deltoid-ovate, acute or subcaudate, somewhat hastate-lobed at the almost truncate base, shallowly dentate,

thin, harsh and slightly scabrous upon both surfaces, 4 to 5 cm. long, half as broad, minutely punctate, slightly pubescent upon the nerves; slender fuscous-pubescent petioles 1 cm. long: heads in rounded axillary and terminal thyrsoid panicles; pedicels filiform, flexuous, covered with fine spreading purple pubescence; bracts and bractlets subulate, minute; involucre turbinate, the lower much reduced scales somewhat decurrent upon the pedicels, the inner scales oblanceolate-oblong, acuminate, erose, puberulent or granular dorsally, thin, striate, often purplish-tinged; flowers about 8: corolla tubular, slightly and gradually narrowed from the summit to the base, essentially glabrous, slightly exceeding the barbellate pappus: achenes dark-colored, upwardly hispid upon the prominent angles. — *E. ageratifolium*, var. *purpureum*, Coulter, Bot. Gaz. xvi. 98 (1891). — Collected by H. von Türckheim in Coban, Depart. Alta Vera Paz, Guatemala, altitude 1,415 m., March, 1887, no. 52 of Mr. John Donnell Smith's sets. This plant differs from *E. ageratifolium*, DC., so greatly in pubescence, leaf-texture, involucre, and inflorescence that intergradation does not appear likely.

EUPATORIUM DASYCARPUM, Gray, Proc. Am. Acad. xxii. 420 (1886). Add syn. *Stevia rapunculoides*, DC. Prodr. v. 124 (1836).

Eupatorium dryophilum. Perennial from a thickish branched caudex; stems several, erect, 5 to 7 dm. high, terete, finely striate, puberulent or tomentulose, slightly scabrous, not glandular, reddish brown, branched at the summit: leaves opposite or ternate, sessile, ovate or oval, the lowest obtuse, the upper acute, all 3-nerved, shallowly few-toothed, thickish, reticulate-veiny, very scabrous upon both surfaces, entirely destitute of glands or resinous particles: heads large, 1.4 cm. in diameter, slender-pedicelled, erect; involucral scales thin, green, oval to oblong, rounded at the apex, 4–5-seriate, striate, glabrous, mealy not viscid: corollas purple, glabrous except at the short-toothed limb: pappus-bristles sordid, barbellate, very unequal; achenes dark olive, 4 mm. long, granular. — Collected by Dr. Edward Palmer, on the Rio Blanco, Jalisco, October, 1886, no. 651, and by C. G. Pringle with oaks and pines on rocky hills near Guadalajara, nos. 2171, 2323. This species is near *E. pleianthum*, Robinson, but differs from it in the absence of resinous globules upon the leaves and the presence of mealiness upon the involucre which is not viscid, also in its shorter darker achenes with fine transverse striation.

EUPATORIUM HYSSOPINUM, Gray, Proc. Am. Acad. xv. 28 (1880). Add syn. *E. koelliaefolium*, Greene, Pittonia, iii. 31 (1896). Identity exact.

Eupatorium Lemmoni, Robinson, Proc. Am. Acad. xxvii. 171 (1892). Add syn. *E. euonymifolium*, Greene, Pittonia, iii. 31 (1896), founded upon a co-type.

Eupatorium Gonzalezii. Apparently herbaceous and to the unassisted vision glabrous throughout; stems terete, green, finely striate, lucid, purple at the nodes, slender; the younger parts microscopically puberulent: leaves opposite, long-petioled, deltoid-ovate, obtuse, coarsely crenate-dentate, 3-nerved from the entire abruptly acuminate base, thin, bright green and glabrous upon both surfaces, 4.5 to 7 cm. long, 4 to 4.5 cm. broad; petioles slender, 3 cm. long; the uppermost leaves ovate-lanceolate, entire, shorter-petioled: heads numerous, about 18-flowered, small, in compound axillary and terminal cymes; peduncles and pedicels ascending, obscurely puberulent; bracts spatulate and mucronate to linear and acute, small; involucral scales green, striate, narrow, linear, obtuse at the scarious erose and often crumpled apex, a few of the outer considerably shorter, ovate, acuminate, ciliolate: corollas white, glabrous throughout, the greenish white proper tube somewhat exceeded by the pure white throat and spreading limb: achene dark, 1.3 mm. long, upwardly hispid on the angles; pappus pure white, sparse; the bristles essentially equal, nearly as long as the corolla, slightly connate into a minute cup at the base. — Collected by Professors C. Conzatti and V. González at El Fortin, Oaxaca, altitude 1,600 m., March, 1897, no. 387.

Eupatorium leonense. Stem 4 mm. in diameter, slightly lignescent, pithy, yellowish brown, glabrate; branches opposite, curved-ascending, striate, tomentulose, finely pubescent: leaves opposite, ovate to deltoid-ovate, long-petioled, thin, coarsely and rather bluntly few-toothed, acutish, abruptly contracted at the entire base to an acuminate attachment to the long petiole, finely pubescent when young, nearly or quite glabrate at maturity, 3 to 5 cm. long, nearly as broad, 3-nerved from a little above the base; petioles 3 to 4 cm. long, pubescent: pedicels slender, flexuous, green, puberulent; bracts minute, subulate; heads rather few in a small round-topped panicle, medium-sized, 8 mm. long, about 12-flowered; involucre campanulate, loosely imbricated, lance-linear, attenuate, very acute, green, striate, thin, sparingly white-pubescent, the outer much shorter: corolla narrowly cylindrical, of essentially uniform diameter throughout its length and without clearly marked throat or proper tube, glabrous: style-branches strongly clavate, yellow; achenes black, glabrous, lucid, 2 mm. long with conspicuous yellow callosity at the base; pappus white, equalling the corolla. — Collected by

C. G. Pringle on the Sierra Madre near Monterey, Nuevo Leon, Mexico, 16 June, 1887, no. 2277.

Eupatorium Liebmannii, Sch. Bip. in Klatt, Leopoldina, xx. 75 (1884). From the characters given and from an excellent drawing (in herb. Klatt) prepared from the original material I cannot avoid the conclusion that this is identical with the earlier *E. hirsutum*, DC., the type of which I have recently examined in the Prodromus Herbarium. The species is represented by Mr. Pringle's no. 6046 from the foothills of the Sierra de San Felipe, Oaxaca.

Eupatorium longifolium. Suffrutescent, 1 m. high: stems virgate, terete, finely striate, covered by a fine spreading purplish and probably viscid pubescence: leaves opposite, short-petioled, ovate-lanceolate, crenate-serrate, 3-nerved, thin, dark green and strigillose (under a lens) above, paler and tomentulose especially upon the veins and veinlets beneath, 1 to 1.2 dm. long, 4 to 5 cm. broad, attenuate to a caudate apex, rounded and deeply cordate at the base, the sinus narrow: inflorescences rounded-corymbose, together forming a large leafy oval or subpyramidal panicle; its branchlets, slender pedicels, and filiform bracts brown-pubescent; heads very numerous, 4 to 5 mm. long, about 10-flowered; involucral scales linear, attenuate, subequal, 3 mm. long, covered with jointed purple hairs and resinous lucid atoms: corolla scarcely 2 mm. long, gradually contracted toward the base, nearly equalled by the simple white pappus: achene dark, minutely pubescent, 1.5 mm. long. — Collected by C. G. Pringle in Tamasopo Cañon, San Luis Potosi, Mexico, 28 November, 1890, no. 3372. This number was distributed as *E. Palmeri*, Gray, to which it is obviously related. It differs, however, both in the nature of its indument and the form of the leaves. The latter are rounded at the base in *E. Palmeri* while in *E. longifolium* they are deeply cordate. *E. filicaule*, Sch. Bip., is also a nearly related species, but its heads are conspicuously racemose, which is not the case here.

Eupatorium lucidum, Ort. Hort. Matr. Dec. 35 (1797). An examination of authentic material of this briefly characterized species shows that it is just the plant to which I have recently assigned the name *E. capnoresbium*, Proc. Am. Acad. xxxv. 331, a name which must accordingly sink into synonymy.

Eupatorium Luxii. Apparently shrubby: branches subterete, striate, covered with a fine spreading and very dark pubescence: leaves opposite, elliptic-ovate (the upper ovate-lanceolate), acute to acuminate at each end, pinnately nerved, 6 to 13 cm. long, half as broad, serrate,

sparingly pubescent when young, quite glabrate except on the nerves and somewhat lucid in age, nigrescent in drying, the teeth salient, mucronulate; petioles 1.8 to 3 cm. long: heads medium-sized, about 25-flowered, 8 to 10 mm. long, in an opposite-branched corymbose panicle; involucral scales 3–4-seriate, ovate to lanceolate, acuminate, closely imbricated externally, nigrescent at the tip, pale at the base, ciliolate, silvery and lucid on the smooth inner surface: corolla-tube 5 to 6 mm. long, glabrous, gradually narrowed from the summit to the base, the teeth very short, sparingly pubescent: achenes 2 mm. long, dark, glabrous, lucid, the angles very prominent; pappus rather copious, white, nearly equalling the corolla. — Collected by Heyde and Lux at Nebaj, Depart. Quiché, Guatemala, altitude 2,150 m., April, 1892, being no. 3387 of Mr. John Donnell Smith's sets of Central American plants, and having been distributed as *E. Tuerckheimii*, Klatt, a species with much narrower leaves and linear-oblong involucral scales, glabrous stem, etc., well shown by no. 77 of Mr. John Donnell Smith's sets.

Eupatorium lyratum, Coulter, Bot. Gaz. xvi. 96 (1891), is *Conyza lyrata*, HBK.

Eupatorium Mariarum. Herbaceous; stems terete, weak, pithy, obscurely pulverulent-puberulent and also covered with scattered spreading white trichomes; branches ascending: leaves opposite, long-petioled, deltoid, acute, coarsely crenate except at the abruptly contracted base, thin, deep green and bearing a few scattered white trichomes above, somewhat paler and essentially glabrous beneath, 3-nerved from the slightly acuminate point of attachment, 5 to 7 cm. long, 4 to 5 cm. broad; petioles weak, flexuous, 3 to 5 cm. long, with a double pubescence as on the stem: heads about 25-flowered, in small axillary and terminal corymbs, pedicellate; bractlets acute, lance-linear to filiform; involucral scales linear-oblong, acute, subequal, thin, mostly 2-nerved, green, 3 mm. long: corolla (probably white) glabrous, with a slender proper tube exceeding a much broader well-marked throat and spreading limb: achenes dark-brown, slightly spindle-formed, hispidulous toward the summit. — Collected by E. W. Nelson on Maria Madre Island of the Tres Marias Group, May, 1897, no. 4244. At first taken for *E. pazcuarense*, HBK., but clearly distinct by its long petioles, different leaf-contour and dentation, also in its pubescence.

Eupatorium pachypodum. Caudex thickish, lignescent, branched; stems annual, one to several, erect, simple to the inflorescence, 3 to 4 dm. high, terete, cinereous-tomentulose: leaves opposite, small, much exceeded by the internodes, ovate to suborbicular, acute, rounded at the

essentially sessile base, serrate, 1.3 to 1.8 cm. long, nearly as broad, green and sparingly pubescent above, covered beneath by a short soft ashy more or less deciduous pubescence, and bearing upon both surfaces golden resinous particles: panicle flat-topped, its slender ascending branches and pedicels (7 to 9 mm. long) grayish-tomentulose; bractlets linear to filiform; heads about 12-flowered, 7 mm. long; involucral scales subequal, oblong, soft-pubescent and pale green upon the outer surface, 3 to 4 mm. long, obtuse: corollas white or at least pale, 4 mm. long, with slender tube somewhat exceeded by the gradually ampliated throat, glabrous: achenes 2 lines long, hispid on the angles, pappus white, equalling the corolla. — Collected by C. G. Pringle on rocky hills near Guadalajara, Jalisco, 26 May, 1891, no. 3718. Distributed as *E. scordonioides*? a species with shrubby perennial stems, deltoid-peltate leaves, etc.

Eupatorium pansamalense. Stem glabrous, rather strongly angled, striate, pithy: leaves opposite or ternate, slender-petioled, rhombic-ovate, caudate-acuminate, acute at the base, mucronate-serrate, thin, pinnately nerved, deep green and nearly glabrous except on the midnerve above, paler and puberulent or tomentulose upon the nerves and veins beneath, 1 to 1.3 dm. long, half as broad; petioles 2 to 3 cm. long: branches of the inflorescence and filiform pedicels fuscous-tomentulose; heads about 35-flowered, very numerous in a round corymbose panicle; scales of the involucre in about 3 series, narrowly oblong, acute to acutish, in a dried state stramineous except a central dark brown streak, the more or less narrowed tips thin, erose: corollas slender, without definitely marked throat, glabrous except near the limb: pappus white, equalling the corolla; achenes very small, scarcely 1.4 mm. long, glabrous. — *E. Tuerckheimii*, Coulter, Bot. Gaz. xvi. 97 and in J. D. Smith, Enum. Pl. Guat. ii. 95, as to no. 1342, not Klatt. — Collected by H. von Türckheim at Pansamalá, Depart. Alta Vera Paz, Guatemala, altitude 1,170 m., April, 1888, no. 1342 of Mr. John Donnell Smith's sets. *E. Tuerckheimii*, Klatt, differs in having much narrower oblong-lanceolate subcoriaceous short-petioled leaves which are quite glabrous upon both sides, paler beneath, and marked by a fine transverse venulation.

Eupatorium pinabetense. Shrub with angled and striate glabrous branches: leaves opposite, lance-oblong, acuminate at each end, mucronulate-serrate, smooth, green and glabrous upon both surfaces, 1 to 1.5 dm. long, 2 to 3 cm. broad, pinnately veined from a strong midnerve: smaller branches of the rather dense thyrsoid panicle fuscous-

tomentulose under a lens; heads numerous, crowded, small, about 10-flowered, short-pedicelled; scales of the involucre very few, unequal, elliptical, rounded at the apex, glabrous but erose-ciliolate, in a dried state brown: corolla glabrous or nearly so even at the limb, without clearly marked throat, equalled by the white pappus: achenes (young) pale, glabrous, 1.8 mm. long. — Collected by E. W. Nelson near Pinabete, Chiapas, Mexico, 8 February, 1896, no. 3785. This species is near but clearly distinct from *E. daleoides*, Hemsl. and *E. tepicanum*, Hemsl.

Eupatorium pleianthum. Doubtless perennial: stem slender, terete, scabrous-puberulent, finely striate, reddish brown, loosely few-branched above: leaves opposite, ovate, essentially sessile, thickish, reticulate-veiny, coarsely few-toothed, acute, cordate, 3-nerved, 2.5 to 3.5 cm. long, two-thirds as broad, slightly scabrous upon both surfaces, covered below by bright resinous globules: heads large, 2 cm. in diameter, slender-pedicelled, erect; involucral scales imbricated in 3 or 4 rows, oval to oblong, rounded at the apex, thin, glabrous and glutinous, striate, pale green, scarcely herbaceous: corollas 6 mm. long, gradually narrowed from the summit to the base, about equalled by the copious stiffish tawny pappus: styles very long and conspicuous, clavate; achenes 5 to 6 mm. in length tapering toward the base, reddish brown, covered with resinous globules, not tranversely striate. — *E. adenospermum*, var. *pleianthum*, Gray, Proc. Am. Acad. xv. 26. — Collected by Dr. Berthold Seemann, Western Mexico. Type in herb. Gray. While sharing many characters with *E. adenospermum*, Sch. Bip., this plant differs so markedly in its opposite (not alternate), shorter, ovate not oblong leaves of differing dentation that intergradation seems very unlikely.

Eupatorium prionobium. Branches ascending, terete, green, striate, puberulent: leaves opposite, petiolate, deltoid, ovate to ovate-oblong, cordate with open sinus and hastate tendency, acutish to rounded at the apex, crenate or crenate-serrate, thickish, bright green but covered with short scattered white hairs upon both surfaces, scarcely paler beneath, 2 to 4 cm. long, 1.7 to 2.5 cm. broad; petiole puberulent, 6 mm. long, sulcate upon the upper side: heads small, about 20-flowered, in round-topped sessile cinereous-puberulent corymbs; pedicels 3 to 5 mm. long; bractlets subulate; involucre green, the scales lance-oblong, acute, subequal, loosely imbricated, 2.5 mm. long, scarcely half the length of the flowers: corolla in dried specimen white, 3 mm. long, with a relatively long throat narrowed into a shorter tube, glabrous, equalled by the bristles of the pappus; these somewhat unequal, barbellate, white

but the barbules upon the lower half tipped with deep purple or violet: achenes 1.8 mm. long, upwardly hispid on the angles. — Collected by E. W. Nelson on the Sierra Madre, State of Chihuahua, Mexico, 29 September, 1899, no. 6499. Type in herb. Gray and herb. U. S. Nat. Museum. Related to *E. ageratifolium*, DC., and *E. occidentale*, Hook.

Eupatorium prionophyllum. Tree; appearing glabrous to the unassisted vision, but covered upon the branchlets, petioles, veins of the leaves, and pedicels by traces of a short close fuscous tomentum; branches curved; cortex gray: leaves opposite, slender-petioled, broadly ovate, conspicuously acuminate, usually obtuse at the base, incisely and often somewhat doubly serrate-dentate nearly from the base to the apex, thin, green on both surfaces, pinnately veined, 7.5 to 9 cm. long, two-thirds as broad; the teeth acuminate, incurved; petioles 1 to 4 cm. long: heads 25–30-flowered, in terminal opposite-branched rounded at first thyrsoid at length more open panicles; bractlets filiform; scales of the involucre imbricated in about 3 series, the outer short and ovate, acute, mucronate with a glandular tip, the inner oblong, obtusish, all striate, fimbriate-ciliolate, externally stramineous becoming purplish or fuscous in age especially near the tip, silvery and lucid within: corolla glabrous, gradually narrowed from the summit to the base: pappus white, barbellate, moderately copious, nearly equalling the corolla: achenes at maturity dark brown, glabrous, lucid. — *E. ixiocladon*, Klatt, Bull. Soc. Bot. Belg. xxxi. 190, not Benth. — Collected by Prof. H. Pittier on the banks of the river Poros, no. 1705 (type in herb. Gray) and near the Rancho Flores, no. 1900, Costa Rica. This species has no close affinity with *E. ixiocladon*, Benth., a plant well shown by Mr. J. D. Smith's no. 7501.

Eupatorium quadrangulare, DC. Prodr. v. 150 (1836). Of this, *E. thyrsoideum*, Moc., notwithstanding its supposed terete stems, is certainly a synonym. Nothing beyond the younger branchlets of *E. thyrsoideum* appears to be known, while even in the square-stemmed *E. quadrangulare* these younger branches are often subterete.

Eupatorium viscidipes. Stem slender, terete, dark-purple, minutely glandular and very viscid; branches opposite, spreading, curved upward: leaves opposite, deltoid-ovate, caudate-acuminate, crenate-serrate in the middle, 3-nerved from the obtuse or subtruncate base, 2.2 to 3.5 cm. long, 1.3 to 2.5 cm. broad, minutely puberulent above, slightly paler and punctate beneath with translucent dots; petioles 1.2 to 1.7 cm. long: heads rather numerous, small, 6 mm. in diameter, about 18-flowered, borne in a large loose corymbose leafy-bracted panicle; pedicels filiform, 3 to

13 mm. long, glandular and very viscid, covered with extraneous particles; involucre turbinate-campanulate; the scales very unequal, much imbricated, pluriseriate, the outer ovate-oblong, the inner oblong, subscarious, striate, all obtuse or rounded at the apex, glabrous or slightly glandular, viscid: corolla glabrous, white, 2.3 mm. long; the proper tube short, much exceeded by the scarcely enlarged cylindric throat: achenes nearly black, columnar, hispidulous on and between the angles; pappus bright white, a little shorter than the corolla. — *E. pycnocephalum*, Coult. in J. Donnell Smith, Enum. Pl. Guat. iv. 75 (1895), as to no. 3397, not Less. — Collected by Heyde & Lux at Chicamán, Department Quiché, Guatemala, altitude 1,230 m., April, 1892, no. 3397 of Mr. J. Donnell Smith's Guatemalan sets. Type in herb. Gray. To be distinguished from *E. pycnocephalum*, Less. by its viscidity, quite different and much more imbricated involucre, etc., and from *E. anisopodum*, described above, by its viscidity, different leaf-form, rounded instead of acute or acuminate involucral scales, etc.

Brickellia amblyolepis. Stem large, fistulose, 2 to 2.5 m. high, glabrous, purple mottled with green: leaves whorled below, opposite above, alternate in the upper parts of the open inflorescence, ovate, acuminate, 3-ribbed from the cuneate entire base, coarsely serrate from below the middle to the acuminate apex, green and glabrous above, paler and finely pubescent upon the veins beneath, 7 to 13 cm. long, half as broad; petioles 1.3 to 3.4 cm. long: heads rather large, broader than high, nodding in an open leafy panicle; pedicels bearing a few linear to spatulate bractlets; scales of the involucre in 3 to 4 series, spatulate-oblong, rounded at the apex, green and nearly glabrous except upon the deep purple tomentulose margin: corollas greenish, 5 mm. long, glabrous, nearly equalled by the rather copious purple-tinged pappus: achenes (immature) 5 mm. long, minutely pubescent; styles strongly clavate, bright orange turning to brown. — Collected by C. G. Pringle on mountains above Iguala, Guerrero, Mexico, 4 October, 1900, no. 8415. A stately species 2 to 3 metres high, not very closely related to any hitherto described. Type in herb. Gray.

Brickellia cardiophylla. Herbaceous; stem terete, glandular-pubescent; branches opposite, widely spreading: leaves ovate-triangular, acute or obtusish, entire or nearly so, broadly cordate at the base, membranaceous, 3-nerved, minutely glandular-puberulent, green upon both surfaces, scarcely paler beneath, 5 to 6 cm. long, nearly as broad; petioles slender, 2 to 3 cm. long: heads subumbellate near the ends of the branches, campanulate, 1 to 1.5 cm. in diameter; pedicels filiform, gland-

ular-puberulent, 2 to 3 cm. long, naked or bearing a single minute lanceolate bract; involucral scales appressed, imbricated in about 5 series, from ovate to linear obtusish, striate, the outer herbaceous-tipped, the inner often purplish; achenes columnar, 2.5 mm. long, minutely roughened or hispid; pappus bright white, not copious, 7 mm. in length: corollas in a dried state cream-colored. — Collected by C. G. Pringle in a barranca near Guadalajara, Jalisco, 1 May, 1894, no. 5885a. Type in herb. Gray. Near *B. floribunda*, Gray, but heads fewer and considerably larger: leaves subentire and of different contour.

Brickellia hebecarpoides. Erect herb, seemingly perennial but root not seen; stem straight, terete, striate, glandular-pubescent, copiously branched above: leaves opposite (the upper with a slight tendency to be alternate), ovate to ovate-oblong, acute or obtuse, membranaceous, finely and regularly serrate (the rameal entire or nearly so), rounded or abruptly acuminate at the 3–5-nerved often oblique base to the slender petiole, puberulent above, glandular-puberulent beneath, both surfaces green, the lower scarcely paler; branches slender, spreading, leafy: peduncles solitary in or usually a little above the forks of the branches, 1 to 2.5 cm. long, filiform, ascending or erect, glandular-pubescent, bractless; involucre 1.2 cm. long, campanulate, its outer bracts lance-oblong, acute, glandular-puberulent, herbaceous or at least herbaceous-tipped, half to two thirds the length of the lance-linear attenuate striate often purplish inner bracts; flowers about 30: corolla 1.3 cm. long, slender, glabrous, purple-tinged at least near the limb: achenes short, only 2 mm. in length, minutely pubescent; style-branches orange, strongly clavate. — Collected by C. G. Pringle in a barranca near Cuernavaca, State of Morelos, Mexico, altitude 1,540 m., 24 June, 1896, no. 7332. Type in herb. Gray. This species is related to *B. hebecarpa*, Gray, but differs in its scarcely pubescent achenes and much longer outer involucral scales, as well as in other ways.

Brickellia petrophila. Compact shrub, 3 to 6 dm. high; stems branched from near the base; branches curved-ascending, becoming erect, gray or lightish brown, covered with a fine spreading pubescence consisting of minute gland-tipped hairs and longer non-glandular hairs, the latter readily distinguishable to the unassisted vision: leaves opposite, small, reniform, ovate, crenate, obtuse, broadly and shallowly cordate at the base, 7 to 10 (rarely 28) mm. long, 1 to 3 cm. broad, somewhat rugose above, finely pubescent or even tomentulose upon both surfaces, but scarcely or not at all canescent: heads subsessile, terminal on short or more elongated branchlets either forming a cylindric racemiform or a

broader and more pyramidal inflorescence, the two forms occurring upon the same individual; involucre cylindric or in a dried state narrowly campanulate, the scales stramineous, striate, imbricated in about four very unequal series, the outer ovate, obtuse, pubescent or at least ciliate, the inner oblong-linear, acute, about 8 mm. long; flowers about 20: achenes columnar, 3 mm. long, olive brown, slightly hispid on the ribs. — Collected by C. G. Pringle on rocky hills near the city of Chihuahua, 13 October, 1885, no. 610 (type, in herb. Gray). To this species I would refer the following specimens: from San Luis Potosi, *Schaffner*, no. 365, *Parry & Palmer*, no. 351; from Guanajuato, *Dugès*, no. 449; from Zacatecas, *Deam*, no. 140; from Durango, *Palmer*, no. 753. This species is nearly related to and has been generally confused with the more southern *B. veronicaefolia*, Gray, a species which is readily distinguishable by the extremely fine canescent non-glandular pubescence of its branchlets, in which the individual hairs cannot be seen without the use of a strong lens. The involucral scales of *B. veronicaefolia* are more closely imbricated and in more numerous rows.

Var. **umbratilis.** Heads larger, 1.5 cm. in diameter, terminal upon more elongated branches. — Collected by Dr. Edward Palmer in a shady ravine at Parras, Coahuila, October, 1898, no. 438, and also a solitary individual in a ravine at Mapimi, Durango, no. 521.

Brickellia vernicosa. Shrub with striate buff or at length gray cortex and erect scabrous-puberulent branches: leaves alternate, ovate, serrate, acutish, bright green, coriaceous, veiny, subsessile, minutely hispidulous, glandular-punctate beneath, often vernicose, 1 to 1.7 cm. long: inflorescences cylindric thyrses 1 to 1.5 dm. long; bracts leaf-like but very small; heads subsessile, 1.2 cm. long, on short branches; involucral scales about 4-seriate, varying from ovate to linear-oblong, obtuse, minutely granular, striate: slender corollas 7 to 8 mm. long, the upper half violet: achenes slender, columnar, light-colored, 4 mm. long, upwardly hispid; pappus copious, 6 mm. long; styles yellow, only moderately clavate. — Collected by Dr. Edward Palmer at Santiago Papasquiaro, Durango, "April and August," 1896, no. 57. Related to *B. baccharidea*, Gray, but readily distinguished by its much longer achenes, etc.

MONTANOA ARBORESCENS, Sch. Bip. (*Montagnaea arborescens*, DC. Prodr. v. 565). An examination of the type shows that the tips of the pales are recurved as in most of the other species of this genus and not inflexed as unfortunately described in the original characterization. The leaves are oblong-lanceolate, attenuate at each end, rather sharply

and regularly serrate near the middle and relatively narrower than in the nearly related *M. frutescens*, Hemsl. I am unable to find *M. arborescens* represented in any of the many recent Mexican collections.

Calea Pringlei. Stems terete, 6 to 9 dm. high, in dried state striate, dull brown, covered with a fine spreading or slightly reflexed tomentum of sordid color, and on young parts somewhat glandular; branches opposite: leaves broadly ovate to nearly orbicular, sessile, acute, coarsely dentate (1 to $1\frac{1}{2}$ teeth to the centimeter), rugose and scabrous-puberulent above, paler green, reticulate veiny, and covered with a fine white crisped pubescence beneath: heads 8 mm. long, 3 mm. in diameter, about 10-flowered, borne on pedicels 2 to 5 mm. long in opposite-branched compound umbelliform cymes; scales of the cylindrical involucre pale yellow, striate, very unequal, rounded at the tip, the outer sparingly pubescent, small, not foliaceous nor even herbaceous; pales erose, nearly or quite glabrous: corolla nearly glabrous but covered with transparent globules, the proper tube slender and somewhat contracted to the summit where it suddenly expands into the very short throat and deeply cleft limb of five linear segments: achenes slender, somewhat attenuate toward the base, dark-colored with a violet tinge, appressed-pubescent; pappus scales about 1 mm. long, also purple-tinged. — Collected by C. G. Pringle on mountains above Iguala, Guerrero, Mexico, altitude 1,230 m., 24 October, 1900, no. 8373. Type in herb. Gray.

CALEA ZACATECHICHI, Schlecht., var. **calyculata.** Involucre subtended at the base by 2 or 3 herbaceous-tipped bracts; these usually shorter than but sometimes exceeding the inner scarious scales. — Mexico, Nuevo Leon in the Sierre Madre near Monterey, *C. G. Pringle*, no. 2224, 16 July, 1888; also in the same locality, *C. & E. Seler*, no. 1080, 12 October, 1895.

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CONTRIBUTIONS FROM THE GRAY HERBARIUM OF HARVARD UNIVERSITY.

NEW SERIES. — No. XXI.

SOME NEW SPERMATOPHYTES FROM MEXICO AND CENTRAL AMERICA.

BY M. L. FERNALD.

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By M. L. Fernald.

Presented March 13, 1901. Received March 20, 1901.

Fimbristylis melanospora. Glaucous, tufted from a hard base: leaves firm, smooth, strongly nerved, 1 to 1.5 mm. wide, tending to become involute, the longest barely 1 cm. long, with a short deltoid cartilaginous tip: culms compressed, with thin edges, 2 dm. or less high: umbel decompound, with very short rays, forming a dense inflorescence 1 to 2 cm. broad; involucre of 2 or 3 very unequal leaves, the longest not equalling the mature umbel; spikelets ovoid-oblong, 3.5 to 4.5 mm. long, 2 to 2.5 mm. thick: scales ovate, blunt, slightly carinate, pale brown with broad white scarious margins: style slender, terete, smooth, with 2 pubescent branches; achenes lenticular, obovoid, broadly rounded above, 1 mm. long, brownish black, minutely muriculate. — Vera Cruz, low grounds, Vera Cruz, April 23, 1894 (*C. G. Pringle*, no. 5773). Superficially resembling some forms of *F. polymorpha*, Boeckl., but differing in the paler and smoother leaves, the broader white margins of the scales, the very different blackish achene, and the slender (not compressed) smooth style.

F. alamosana. Low tufted annual, about 1 dm. high: leaves flat, smooth, mostly much shorter than the slender flexuous culms, rarely longer; the sheaths densely ciliate: umbels decompound, with 3 to 7 slender lax unequal rays, the longest 2 or 3 cm. long, the spikelets mostly long-pedicelled; involucre of 2 or 3 unequal leaves, the longest equalling or exceeding the rays; spikelets pale straw-colored or whitish, ovoid-oblong, acutish, 2.5 to 3.5 mm. long, 1 to 1.75 mm. thick: scales ovate, acutish, or the lowest mucronate, slightly carinate: style compressed, pubescent, with 2 branches; achene barely 1 mm. long, broadly cuneate-obovoid, with 10 or 12 obscure longitudinal bands, white, pearly and finely muriculate all over. — Sonora, Alamos, Sept., 1890 (*Edw.*

Palmer, no. 699). Differing from *F. laxa*, Vahl, in its paler smaller spikelets and smaller white and glossy achenes.

F. Holwayana. Culms slender, 1 to 3 dm. high, much overtopping the pale green narrow (0.75 mm. wide) ciliate leaves: umbel simple, with 2 (rarely 1) to 4 ovoid-oblong spikelets 6 to 8 mm. long, 2.5 to 3.5 mm. thick, the middle (or rarely solitary) one sessile, the others on slender ascending rays 0.5 to 2 cm. long; involucre of 2 or 3 ciliate leaves, the longest one usually much exceeding the rays: scales from orbicular to ovate, blunt, castaneous and shining, the green midrib in the outer somewhat prolonged into a short awn, in the others barely into a cusp: achene short-stipitate, pearly, broadly obovoid, subtruncate above, half as long as the scale, 1.25 mm. long, nearly as thick, with about 16 longitudinal ribs, and many linear transverse markings; style flat, fimbriate, exserted. — JALISCO, Chapala, Sept. 18, 1899 (*E. W. D. Holway*, no. 3443). Closely related to *F. pentastachya*, Boeckeler, but differing in its narrower spikelets and broader scales, and in the achenes which are smooth or with one or two tubercles at the very summit, not tuberculate-roughened throughout as in *F. pentastachya*.

F. obscura. Glaucous, loosely tufted from slender branching caudex: leaves flat, 2 or 3 mm. wide, the longest 1.5 dm. long, smooth, or the margins ciliolate-scabrous except at the acutish cartilaginous tip: culms compressed, with thin edges, 4 dm. or less high: umbel decompound, with 2 to 4 rays 2 or 3 cm. long and several shorter ones; involucre of 2 leaves much shorter than the umbel; spikelets mostly pedicelled, or rarely 2 or 3 fascicled and sessile, lanceolate, acute, 5 to 8 mm. long, 1.5 to 2 mm. thick: scales dark brown, ovate-oblong, strongly carinate and mucronate: style slender, terete, smooth, with 3 pubescent branches; achenes trigonous with obtusish angles, obovoid, barely 1 mm. long, whitish, with extremely obscure longitudinal markings (seen only under strong magnification). — DURANGO, alkaline bottoms near Durango, June, 1896 (*Edw. Palmer*, no. 186): SAN LUIS POTOSI, in the mountains, San Miguelito, 1876 (*Schaffner*, no. 558). Resembling *F. autumnalis*, R. & S., but clearly differing in its caespitose perennial habit, and its larger, paler, and duller achenes.

GLYPHOSPERMA PALMERI, Watson, Proc. Am. Acad. xviii. 164. Mr. Pringle calls attention to the fact that this plant, which in Mexico appears like an introduced species, is identical with the Old World *Asphodelus fistulosus*, L.

Cologania Deamii. Stems slender, 1.5 to 2 dm. long, from a slender creeping rootstock, ascending and branched, the tips flexuous but

slightly twining, covered with fuscous retrorse-hispid pubescence: stipules ovate to lanceolate, 4 to 6 mm. long: petioles retrorse-hispid, 1.5 to 2.5 cm. long; leaflets oblong-ovate to obovate, mucronate, slightly strigose above, pale and hispidulous beneath, 2 to 4 cm. long, the terminal on a petiolule (0.5 cm.) thrice as long as those of the lateral leaflets: umbels 3–6-flowered, the principal peduncles 4 to 6 cm. long, retrorse-hispid, those on the flexuous branches shorter; pedicels 1 to 1.75 cm. long: calyx 1 to 1.2 cm. long, hispid: corolla violet, 2 to 2.5 cm. long. — MORELOS, Cuernavaca, July 7, 1900 (*C. C. Deam*, no. 40). Unique in its long peduncles.

Platanus glabrata. Leaves from broad-cuneate to subcordate, unequally 5–9-lobed, the middle lobe and the upper pair of lateral ones long-acuminate, the lower ones short-acuminate; the margin entire; at first closely cinereous-tomentose beneath, soon becoming glabrate: peduncles 0.5 to 1 dm. long, bearing 1 or 2 heads 1.5 to 2 cm. in diameter. — *P. Lindeniana*, Wats. Proc. Am. Acad. xviii. 155, not Mart. & Gal. — COAHUILA, Monclova, Aug., 1890 (*Edw. Palmer*, no. 1269); Saltillo, April 5, 1887 (*C. S. Sargent*); by streams near Diaz, alt. 216 m., April 24, 1900 (*C. G. Pringle*, no. 8319). Differing much from *P. Lindeniana* of southern Mexico, which has the less lobed leaves permanently cinereous beneath, and the heads more numerous.

CROTON PALMERI, Watson, var. **ovalis.** Leaves oval, 1.5 to 3 cm. broad, not lanceolate, rounded at base: clusters many-flowered. — NUEVO LEON, Monterey, Oct. 11, 1895 (*C. & E. Seler*, no. 1047).

Alcoceria, nov. gen. of *Euphorbiaceae* (*Hippomaneae*). Monoecious. Staminate flowers in a terminal ament; the individual flowers slightly imbedded at base by close dense pubescence. Calyx of staminate flower with 2 broad fleshy valvate sepals and a third narrow inconspicuous one. Stamen solitary; filament thick, columnar; anther 2-celled, longitudinally dehiscent, dorsally affixed toward the sheathing tip of the filament. Calyx of pistillate flower with three deltoid-subulate teeth and few or no intermediate small glands. Ovary depressed-globose, subtrigonous, the three 1-ovulate cells alternating with the calyx-teeth. Style cylindric, erect, equalling the three recurved branches. Fruit a 3-locular capsule. Seed pisiform, scarcely carunculate. — Dedicated to Gabriel Alcocer, acute observer, teacher in the Escuela Preparatoria, and botanist at the Museo Nacional and the Instituto Medico Nacional of Mexico.

A. Pringlei. Slender shrub, 3 to 5 m. high, the sprawling branches herbaceous, striate, the lower nodes remote: leaves pilose or glabrate beneath, reniform, acuminate, varying from 0.4 to 1.3 dm. long, and from

entire to more or less palmately 3–7-lobed, palmately 5-nerved, the nerves conspicuous beneath; petioles 1.5 to 4 cm. long, pubescent at tip: inflorescence axillary or terminal; the staminate ament linear-oblong, 2 cm. long, long-peduncled, with few strongly reflexed pistillate flowers at base; pedicel of pistillate flower glandular at base, thick-clavate, 1 to 2 cm. long: capsule about 1 cm. broad. — GUERRERO, limestone mountains above Iguala, alt. 1,230 m., Sept. 26, 1900 (*C. G. Pringle*, no. 8433).

Related to *Dalembertia*, Baillon, which differs in the single bract (instead of a 3-lobed calyx) at the base of the anther. Also approaching *Tetraplandra*, Baillon, and *Maprounea*, Aublet, but the formèr is distinguished by its four terminal anthers, and the latter by its short staminate spike and two more or less connate stamens.

Euphorbia (Anisophyllum) puberula.[1] Branching from the base, the branches subligneous, ascending, 2.5 dm. or less high, puberulent, the tips canescent and tomentulose: leaves rhomboidal, 1 to 2 cm. long, 0.5 to 1 cm. broad, very oblique, glaucous beneath, blunt, crenate-serrate, sparingly pilose; stipules setaceous: cymes dense, 1 or 2 cm. broad, terminating the leafy branches: involucre white-pilose, turbinate-campanulate, 1.5 to 2 mm. long, with deltoid hairy lobes; glands 4, short-stipitate, with or without narrow appendages; false gland absent from the broad shallow sinus: capsule appressed-pilose, subacutely lobed, 1.5 mm. long: seed pulverulent, 1 mm. long, oblong or ovoid-oblong, quadrangular, with somewhat broken ridges between the angles. — Mexico without locality (*Coulter*, no. 1438 in part): GUANAJUATO, hills of Guanajuato, 1895 (*A. Dugès*): MORELOS, Puente de Ixtla, July 3, 1900 (*Charles C. Deam*, no. 26); Huerta de la Hacienda de Miacatlan, Distr. Tetecala, Dec. 28, 1887 (*C. & E. Seler*, no. 341): OAXACA, near Mitla, Distr. Tlacolula, June, 1888; Tecomavaca, Nov. 15, 1895; Tomellin, Distr. Cuicatlan, Nov. 15, 1895 (*C. & E. Seler*, nos. 31, 1360, 1376); mountains of Oaxaca, alt. 1,750 m., July–Aug., 1900 (*C. Conzatti & V. González*, no. 1042): CHIAPAS, Ocozuquauhtla, Distr. Tuxtla, Feb. 19, 1896 (*C. & E. Seler*, no. 1952). Nearest related to *E. pilulifera*, L., and *E. lineata*, Watson, differing from the former in its terminal cymes and blunter leaves, from the latter in its rather stouter habit and more rhomboidal leaves, and from both in its cinereous puberulence.

[1] In the preparation of the descriptions of these Euphorbias the writer has been greatly assisted by Professor C. F. Millspaugh, who has generously examined the specimens, and who has already pointed out (Bot. Gaz. xxv. 13) the importance of the involucral appendages in differentiating the species of this genus.

E. (Anisophyllum) potosina. Ascending annual, branching from the base: stems glabrous, or the younger parts minutely pilose, 2 dm. high: leaves 1 to 1.75 cm. long, oblong, oblique, rounded or subtruncate at base, bluntish at tip, glabrous, pale green above, glaucous beneath, the margin coarsely appressed-crenulate; stipules deltoid-acuminate, laciniate: flowers few in small mostly terminal clusters: involucre pyriform, glabrous; the lobes elongate-triangular, entire or nearly so, the 2 flanking the broad rounded sinus much larger and lacerate; glands 4, long-stipitate; appendages very narrow or wanting; false gland aristate, rising from the base of the sinus: capsule glabrous, ellipsoidal, 2.5 to 3 mm. broad, barely 2 mm. high, the three lobes rounded: seed short-oblong, subquadrate, 1.5 to 1.75 mm. long, the dorsal angle prominent, the ventral suppressed, blackish, pulverulent, the angles and the margins of the unequal honeycomb-pits paler. — San Luis Potosi and adjacent Tamaulipas. SAN LUIS POTOSI, without locality, 1876 (*J. G. Schaffner*, no. 856, in part); region of San Luis Potosi, alt. 1,850 to 2,460 m., 1878 (*Parry & Palmer*, no. 814, in part): TAMAULIPAS, near Tula, Sept. 21, 1898 (*E. W. D. Holway*, no. 3200). — Related to *E. hypericifolia*, L., *E. Preslii*, Guss., and *E. brasiliensis*, Lam., but differing in its fewer flowers, larger capsule, and much larger differently marked seed.

E. (Anisophyllum) interaxillaris. Perennial, with slightly woody base: stems prostrate or slightly ascending, 1 dm. or so long, pilose with more or less spreading hairs: leaves short-petioled, oblong or obovate-oblong, oblique, rounded at each end, 0.5 to 1 cm. long, 4 to 7 mm. wide, minutely crenulate, mostly purple-tinged or blotched, sparingly pilose on the margins when young, soon glabrate; stipules narrowly triangular, fimbriate: flowers solitary, a single one accompanying each pair of leaves, on slender pedicels 2 or 3 mm. long: involucre campanulate, 1.5 mm. long, glabrous outside; the lobes triangular, about equal, hairy within; glands 3 or 4, brownish, mostly with suborbicular white appendages 1 mm. in diameter; the 5th gland replaced by an elongated false-lobe at the base of the shallow triangular sinus: ovary glabrous. — MORELOS, Puente de Ixtla, July 3, 1900 (*Charles C. Deam*, no. 25). Related to *E. stictospora*, Engelm., but less pubescent and with solitary flowers.

E. (Zygophyllidium) muscicola. Caudex tuberiform, globose or oblong, 3 to 5 cm. long, narrowed above to a cylindric neck; stem very slender, branching from near the base, the slender flexuous subsimple or slightly forked branches 2 or 3 dm. long, glabrous: lower leaves suborbicular to ovate, rounded or blunt; the upper elliptic-lanceolate, 0.5 to

1.5 cm. long, mucronate, entire or appressed-serrulate, glabrous or sparingly pilose-setulose; the lower equalling the capillary petioles, the upper short-petioled: flowers few, terminal and axillary, on pedicels 2 cm. or less in length: involucre short-campanulate, 2 mm. long, appressed-setulose, the deltoid-oblong truncate erose lobes incurved; glands 4, dark, with pale oblong-lanceolate blunt appendages 1 to 1.5 mm. long; false gland similar: capsule rugulose, 4 mm. high: seed oblong-ovoid, minutely puncticulate, gray or gray-green, mottled with olive or brown. — MORELOS, on mossy ledges of Sierra de Tepoxtlan, alt. 2,310 m., Sept. 12, 1900 (*C. G. Pringle*, no. 8443).

E. (**Cyttarospermum**) **calcicola.** Annual, freely branching, 5 or 6 dm. high, the slender stem and branches viscid-setulose with long pale hairs: leaves broad-ovate, rounded or bluntish at tip, truncate or subcuneate at base, the lower 2 cm. long, the upper much smaller, setulose on both faces, dark above, pale beneath, about equalling the capillary petioles: flowers axillary on capillary pedicels 1 to 1.5 cm. long: involucre broad-campanulate, green and yellow, 1 mm. long, the short incurved cuneate lobes lacerate; glands 4 with 3 finger-like appendages; the false gland slightly larger, with 4 appendages: ovary glabrous. — GUERRERO, limestone mountains above Iguala, alt. 1,230 m., Oct. 5, 1900 (*C. G. Pringle*, no. 8398). Closely related to *E. astroites*, F. & M., but the stem conspicuously setulose, and the pedicels much longer.

E. LANCIFOLIA, Schl., var. **villicaulis.** Stems more or less villous with crisp jointed hairs: leaves rhombic-ovate, acutish, green and lucid above, pale and more or less villous beneath: involucre campanulate, pilose or glabrate, 3 or 4 mm. long; lobes truncate, serrate; glands 1 or 2 associate, hoof-shaped; false glands 3, columnar, truncate, one-third longer than the lobes: capsule (young) pilose, 5 mm. long, with rounded lobes: seed (young) short-oblong, 2 or 2.5 mm. long, pale brown. — CHIAPAS, mountain-slope above Ocociugo, March 13, 1896 (*C. & E. Seler*, no. 2214). Distinguished from the species by its pubescence, involucral lobes, and false glands. In *E. lancifolia* the involucral lobes are fimbriate, equalling or slightly exceeding the subulate false glands.

Pernettya ovata. Branches pale brown, minutely puberulent or glabrate: leaves ovate, short-petioled, 1 to 1.5 cm. long, pale and minutely canescent-tomentulose toward the rounded base; margins finely appressed-serrate, the youngest glandular-ciliate, as are the lower faces of the young leaves: inflorescences axillary, subsessile, all the parts glabrous, the deciduous bracts sometimes with erose margins: flowering calyx 3 mm. long, cleft half-way to the base into deltoid smooth-

edged lobes: corolla ovate-campanulate, 6 or 7 mm. long. — CHIAPAS, mountain woods between San Cristóbal Las Casas and Huitztan, March 10, 1896 (*C. & E. Seler*, no. 2126[b]). Growing with *P. ciliaris*, Don, but nearer related to *P. coriacea*, Klotzsch, from which it differs in its pale and minutely puberulent branchlets, paler leaves and glandless calyx.

Arctostaphylos Conzattii. Shrub with smooth reddish bark easily peeling from the branches: leaves oblong-oblanceolate, acute, 2 to 4 cm. long, 0.75 to 1.5 cm. wide, entire and subcuneate below to a short petiole, sharply serrate above the middle, smooth and sublucid above, sparingly sordid-pilose beneath: racemes terminal, panicled, 1 dm. or less long; the rachis, pedicels and short ovate-lanceolate bracts puberulent; pedicels 1–3-bracted, 1 cm. long: calyx puberulent, with ovate bluntish lobes: corolla urceolate, glabrous, 5 or 6 mm. long. — OAXACA, Sierra de San Felipe, alt. 3,000 m., April 7 and 8, 1898 (*C. Conzatti*, no. 691). In its inflorescence resembling *A. rupestris*, Robinson & Seaton, but differing in its much smaller but more coarsely toothed leaves.

A. glabrata. Shrub with smoothish gray-brown bark; the young branches reddish-brown: leaves narrowly elliptic-oblong, acute or blunt, 2 to 4 cm. long, about 1 cm. wide, tapering to short thick petioles 3 or 4 mm. long, entire or sharply serrate with short mucronate teeth, bright green above, paler beneath, ferrugineous-tomentulose when young, becoming glabrate: racemes simple, terminal or axillary, 2 or 3 cm. long; the rachis, the lance-acuminate bracts, and the short (3 to 5 mm. long) pedicels ferrugineous-tomentose, rarely a little glandular: calyx slightly tomentulose, the lobes broadly deltoid: corolla urceolate, glabrate, 4 or 5 mm. long: berries dark, 6 or 7 mm. in diameter. — OAXACA, ledges at the summit of Sierra de San Felipe, alt. 3,500 m., Sept. 25, 1894 (*C. G. Pringle*, no. 5712), Aug. 15, 1897 (*C. Conzatti & V. González* in Exsicc. Conzatti, no. 409); mountains about Yalalag, alt. 1,850 m., Aug. 1. 1894 (*E. W. Nelson*, no. 973). Related to *A. arguta*, Zucc., but differing in its shorter leaves, and shorter simple essentially glandless raceme.

Parathesis chiapensis. Branches stout, gray and smoothish, the younger parts closely tomentose with short stellate ferrugineous hairs: leaves elliptic, 1.5 to 2 dm. long, narrowed above to a short slender acumen and below to a thick cinereo-ferrugineous petiole 0.5 to 1 cm. long; margin closely and finely crenate-dentate; upper surface smooth and dull, the lower ferrugineous-tomentose when young, becoming glabrate: panicle terminal, leafy below, in anthesis 1.5 dm. high, pyramidal, the spreading branches 3 to 6 cm. long, bearing many-flowered

corymbs, rusty tomentose and finely linear-maculate throughout; bracts lanceolate, 5 mm. long; pedicels thickish, somewhat clavate, becoming 1 to 1.5 cm. long: calyx in anthesis 3 or 4 mm. long, deeply cleft into 5 linear lobes: corolla-lobes lanceolate, 6 mm. long, strongly recurved, tomentulose within: filaments broad at base, 2 mm. long; anthers oblong-lanceolate, 3 mm. long. — CHIAPAS, in mountain-woods between San Martin and Ococingo, March 13, 1896 (*C. & E. Seler*, no. 2226). Related to *P. sessilifolia*, Donnell Smith, but differing in its crenate dull leaves, closer shorter pubescence and larger flowers.

Evolvulus Seleriana. Perennial: stems prostrate or slightly ascending, 1 to 2 dm. long, slightly branched, silky pilose, the older becoming glabrate: leaves obcordate, obovate or obovate-oblong, short-petioled, 5 to 12 mm. long, above appressed long-sericeous or glabrate, beneath permanently sericeous: flowers axillary, the filiform arcuate sericeous peduncles bractless, 9 to 13 mm. long: calyx very pubescent, 4 mm. long, with lanceolate lobes: corolla pale (apparently white) somewhat silky without, 8 to 9 mm. high. — CHIAPAS, Tuxtla, Feb. 19, 1896 (*C. & E. Seler*, no. 1926). Nearest related to *E. nummularius*, L., but with different pubescence, obcordate leaves, longer peduncles, and larger flowers.

Ipomoea caudata. Slender glabrous vine: leaves on slender petioles 3 to 5 cm. long; blade 1 dm. or less long, narrowly ovate, prolonged into a caudate-acuminate tip, the base rounded-sagittate, the basal lobes varying from blunt to acuminate, dark green above, glaucous beneath, palmately 7-nerved at base: peduncles slender, 1 to 1.5 dm. long, simple or once forked at the tip; pedicels 2 to 4 cm. long: calyx narrowly oblong, 1 cm. long, the unequal oblong blunt lobes mottled: corolla rose-purple, 0.5 dm. long, the cylindric tube 4 cm. long, the short spreading limb 2 cm. broad: style filiform, glabrous. — MORELOS, on mossy faces of the knobs of the Sierra de Tepoxtlan, alt. 2,310 m., Sept. 5, 1900 (*C. G. Pringle*, no. 8448). Habitally resembling *I. simulans*, Hanbury, but with longer peduncles and calyx, and more slender corolla.

Cordia (Sebestenoides) Seleriana. Branches straggling, covered with brown verrucose bark: leaves ovate or suborbicular, 1 to 2 cm. long, pulverulent and hispidulous; petioles slender, hispid, 3 or 4 mm. long: corymbs few-flowered, the parts very hispid; peduncles 2.5 cm. or less in length: calyx oblong-campanulate, 1 cm. long, with short rounded lobes: corolla 3 cm. long, somewhat hispidulous below, the thin ovate-oblong round-tipped crenulate lobes 1 to 1.5 cm. long. — OAXACA, dry

woods, Huilotepec, Tehuantepec, Jan. 20, 1896 (*C. & E. Seler*, no. 1779).

Salvia (Micranthae) ageratifolia. Tall branching annual, the sharply quadrangular herbaceous stems long-setulose, with somewhat shorter gland-tipped hairs intermixed: leaves cordate, ovate or deltoid-ovate, 2 to 4 cm. long, coarsely crenate, bluntish, dark green and minutely pilose or glabrate above, glaucous and puberulent beneath; petioles slender, 1 to 3 cm. long, more or less setulose: racemes simple, elongated, becoming 2 dm. long; verticels 2–4-flowered, the lower 1.5 to 2 cm. apart; bracts persistent, ovate-acuminate, 2 mm. long; pedicels becoming 3 mm. long: calyx at first narrowly later broadly campanulate, in anthesis 5 or 6 mm. long, 2 or 3 mm. broad, in fruit 8 or 9 mm. long, 4 or 5 mm. broad, setulose, the entire mucronate upper lip slightly shorter than the narrower acuminate lower lobes: corolla 7 or 8 mm. long, blue, the tube included, the pilose galea shorter than the lip. — OAXACA, mountains near Oaxaca, alt. 1,750 m., July, Aug., 1900 (*C. Conzatti & V. González*, no. 1049). Closely related to *S. micrantha*, Vahl, & *S. setosa*, Fernald (nos. 8 & 9 of the writer's Synopsis[1]). From the former quickly separated by its loose elongated raceme and setulose stem; from the latter by its cordate leaves, setulose stem, and scarcely secund racemes.

S. TILIAEFOLIA, Vahl, var. **rhyacophila.** Stem (especially above), petioles, and calyces densely villous: leaves more pubescent than in the species. — MORELOS, lava-fields below Cuernavaca, alt. 1,230 m., Oct. 17, 1900 (*C. G. Pringle*, no. 8381).

S. (Angustifoliae) setulosa. Tall (about 1 m. high) and erect shrub with stiff ascending branches; stem and especially the young branches setulose with long white hairs: leaves rhombic-oblong to deltoid, blunt, cuneate at base into slender petioles, 2 to 4.5 cm. long, 1 to 2.5 cm. broad, dark green and sparingly pilose above, pale and more or less pilose beneath, the margin finely crenate-serrate: peduncles 1 to 1.5 dm. long, sparingly setulose or glabrate: racemes becoming 2 dm. long; the ovate long-acuminate puberulent bracts 1 to 1.5 cm. long, long-ciliate on the margins, tardily deciduous: verticels 6–10-flowered, becoming remote, the lowest 3 or 4 cm. apart; pedicels 2 to 4 mm. long, canescent with appressed pubescence: calyx in anthesis 7 mm. long, hirsute especially on the tube, the ovate-lanceolate long-subulate lobes about equalling the tube, the upper lip usually tridentate: corolla deep blue, 18

[1] Proc. Am. Acad., xxxv. 489–556.

to 20 mm. long, the scarcely ampliate tube twice exceeding the calyx; the pilose lips subequal: style densely bearded. — MORELOS, mountains above Cuernavaca, alt. 2,460 to 2,620 m., Oct. 13, 1900 (*C. G. Pringle*, no. 8403), Sept. 1, 1900 (*C. G. Pringle*, no. 9204). Closely related to *S. prunelloides*, HBK. (no. 40 of the writer's synopsis), but differing from that and the other members of the group in its tall erect stem.

S. (Vulgares) igualensis. Tall (1 m. or more high), the strongly grooved quadrangular stem canescent with close pubescence: leaves broad-ovate, the lower suborbicular, short-acuminate, rounded at base, 5 to 7 cm. long, 4 to 5.5 cm. broad, coarsely crenate-serate, minutely puberulent or glabrate on both faces, pale beneath, on slender canescent petioles 1 cm. or less in length: racemes long and slender, becoming 1.5 to 2 dm. long; verticels 10–20-flowered, mostly approximate, the lower 1.5 cm. apart; bracts lanceolate, caducous; pedicels becoming 2 mm. long: calyx in anthesis about 3 mm. long, short-pilose-hispid on the nerves, with short deltoid teeth; corolla blue, pilose, 1 cm. long; the slightly ventricose tube twice exceeding the calyx; galea and lip subequal: style bearded. — GUERRERO, limestone mountains above Iguala, alt. 1,230 m., Sept. 26, 1900 (*C. G. Pringle*, no. 8418). Related to *S. brachyodonta*, Briq. (no. 59 of the writer's Synopsis) and *S. Ghiesbreghtii*, Fernald (no. 60). From the former distinguished by its coarser habit, cinereous stem, short petioles and appressed teeth of the leaves, and shorter pedicels; from the latter by its coarser habit, and broader glabrate leaves without the characteristic lanate pubescence of *S. Ghiesbreghtii*.

S. (Scorodoniae) Dugesii. Shrub, the branches canescent with closely matted simple hairs: leaves oblong or oblong-ovate, 2 to 4 cm. long, rounded at base, acute or bluntish at tip, strongly rugose, green above, canescent beneath with close simple hairs; petioles slender, 1.5 cm. or less long: racemes becoming 1 dm. or so long, simple; verticels 8–12-flowered, the lowest 1 to 1.5 cm. apart; pedicels at most 1 mm. long: calyx cuneate-campanulate, canescent with short mostly simple appressed hairs, in anthesis 7 mm. long, with short flaring blunt or merely short-subulate lobes: corolla 1.5 cm. long, pubescent with short gland-tipped hairs. — GUANAJUATO, Aug., Sept., 1900 (*A. Dugès*). This plant, known as "*Chia cimarona*," is nearest related to *S. lasiantha*, Benth. (no. 104 of the writer's Synopsis), but is distinguished by its narrow leaves, shorter pubescence throughout, larger calyx, and by the pubescence of the corolla, which in *S. lasiantha* is pilose and essentially glandless.

S. LEUCANTHA, Cav., forma **iobaphes.** Calyx and corolla both deep violet. — MORELOS, on ledges of the Sierra de Tepoxtlan, alt. 2,310 m., Oct. 14, 1900 (*C. G. Pringle*, no. 8402).

S. (Macrostachyae) albicans. Shrub 3 to 5 m. high, the branches cinereous-puberulent: leaves elliptic-ovate, acuminate, rounded or subcuneate at base, 4 or 5 cm. long, 2 to 2.5 cm. wide, rugulose, minutely canescent-puberulent, becoming glabrate; the margin finely appressed-serrate; petiole slender, canescent, 1 cm. or less long: racemes 3 to 10 cm. long, the verticels about 10-flowered, mostly crowded, the lower becoming 1.5 cm. apart; bracts thick and firm, densely cinereous-tomentose, ovate, acuminate, 1 to 1.5 cm. long, semi-persistent, the earliest finally deciduous: calyx cuneate-campanulate, densely white tomentose, in anthesis 8 mm. long, the short broad lobes slightly unequal, the longer upper one acute, the lower blunt: corolla 14 mm. long, canescent without; the narrow galea and the tube whitish, the broad lip deep blue: style densely bearded. — GUERRERO, limestone mountains above Iguala, alt. 1,230 m., Sept. 14, 1900 (*C. G. Pringle*, no. 8430). Nearly related to *S. Shannoni*, Donnell Smith (no. 128 of the writer's Synopsis), but the smaller thinner leaves, not tomentose beneath, and the inflorescence more canescent.

S. SESSEI, Benth. Mr. Pringle's nos. 7065 and 7080, from Cuernavaca, cited under *S. pubescens*, Benth., are not that species, but are better placed with *S. Sessei*. Mr. Pringle's no. 8378 is also referable to the latter species.

Monarda Pringlei. Simple, about 1 m. high, the stem obtusely angled, minutely and sparingly puberulent above: leaves thin, lanceolate, 7 to 9 cm. long, 1.5 to 2.5 cm. wide, subtruncate at base, the lower half rather coarsely appressed-serrate, the elongate-acuminate upper half entire, minutely puberulent on both faces, slightly paler beneath; petiole slender, puberulent, 0.5 cm. long: the glomerule terminal, 12–15-flowered; bracts like the foliage-leaves, but smaller and entire; bractlets filiform, often equalling the calyces: calyx 10 or 12 mm. long, cylindric, slightly curved, puberulent, with subulate spreading teeth 2 or 3 mm. long, and numerous crisp ascending shorter hairs in the throat: corolla vermilion, 4.5 cm. long, the slender tube long-exserted, tapering gradually to the ampliate curved throat; lips subequal, 1.5 cm. long, the narrow galea sparingly pilose. — NUEVO LEON, moist wooded cañon near Monterey, June 14, 1888 (*C. G. Pringle*, no. 2199). A handsome plant related to *M. didyma*, L., but differing in its simple habit, minute puberulence, narrow leaves, and fewer flowers.

Physalis puberula. Annual?; puberulent throughout with fine appressed or incurved white hairs: branches slender, terete below, angulate above: leaves ovate, subentire or slightly sinuate, 3 to 7.5 cm. long, 1.5 to 4 cm. broad, acuminate at tip, rounded or subcordate at base; petioles slender, 1 to 4 cm. long: peduncle 0.5 to 1 cm. long, straight but soon recurved: calyx in anthesis 6 to 8 mm. long, the deltoid-lanceolate acuminate lobes equalling the tube: corolla 1.5 to 2.5 cm. broad, sulphur-yellow with brown patches at centre: anthers yellowish: fruiting calyx ovate, 2.5 to 3 cm. long, obscurely 5-angled, slightly sunken at base, the connivent deltoid-lanceolate teeth 0.7 to 1 cm. long. — MEXICO, Sacro Monte, Amecameca, Aug. 31, 1900 (*C. G. Pringle*, no. 9147); Guadeloupe, Aug. 9, 1865–6 (*Bourgeau*, no. 724): DURANGO, Durango, 1896 (*Edw. Palmer*, no. 348). Somewhat resembling the northern *P. philadelphica*, Lam., but with persistent close pubescence and more ovate leaves. Mr. Pringle's plant was accidentally distributed as *P. Pringlei* (with incorrect authority), a name belonging to a very different plant with long glandular pubescence.

SOLANUM ROSTRATUM, Dun., var. **subintegrum.** Leaves sparingly pubescent above, shallowly sinuate-lobed, not pinnatifid: otherwise as in the species. — MEXICO, Tacuba, valley of Mexico, Sept. 18, 1900 (*C. G. Pringle*, no. 9268).

Ruellia (Physiruellia) cupheoides. Slender shrub, 1 to 1.5 m. high, the quadrangular verrucose branches covered with gray bark, the younger parts pilose: leaves elliptic-ovate or ovate-oblong, 3 to 5 cm. long, short-acuminate, pilose, on slender petioles 0.5–1 cm. long: peduncles axillary, divergent, slender, pilose and verrucose, 2 to 6 cm. long, terminated by a single flower or branching and bearing 2 flowers; bracts 2, linear-spatulate, in age becoming 1.5 cm. long: calyx pilose, 1.5 to 2 cm. long, cleft two-thirds to the base into lanceolate or ovate-lanceolate acuminate ciliate lobes: corolla tubular, 3.5 cm. long, yellow or reddish, with short erect blunt greenish lobes; the slightly narrowed tube shorter than the calyx: stamens subequal, included; filaments glabrous; anthers linear-oblong, 4 or 5 mm. long: style bearded; capsule oblong-obovoid, short-pointed, equalling the calyx, glabrous; seeds four, thin, ovate, 0.5 cm. long, dark, with narrow pale margin. — GUERRERO, limestone mountains above Iguala, alt. 1,230 m., Sept. 27, 1900 (*C. G. Pringle*, no. 8409).

Valeriana retrorsa. Slender, 2 to 4 dm. high, from a small oblong tuber; stem densely retrorse-hispid below, glabrous above: leaves 3 to 5 cm. long, the basal short-petioled, the upper sessile; leaflets 3 to 5 pairs, linear-lanceolate, blunt, the lowest pair minute, the terminal leaflet much

larger, often 3 cm. long, mostly entire: inflorescence 3 to 6 cm. high, a trichotomous loose cyme; flowers rather crowded at the tips; floral leaves linear: corolla funnel-form, 6 mm. long, the lobes barely 1 mm. long: stamens and style slightly exserted: fruit hirsute. — MORELOS, mossy rocks, Sierra de Tepoxtlan, alt. 2,310 m., Sept. 5, 1900 (*C. G. Pringle*, no. 8454). Resembling *V. mexicana*, DC., but with hispid stem, narrower leaves, and longer corolla.

Lobelia regalis. Stem tall and stout, softly white-tomentose, almost lanate, above: leaves lanceolate to ovate-oblong, 1 to 2 dm. long, 4 to 8 cm. broad, subentire or minutely denticulate with pale hard teeth, pale green above, at first tomentulose, later glabrate, densely canescent-tomentose beneath; petioles slender, canescent, 2 or 3 cm. long: peduncles white-tomentose, axillary, ascending, becoming 5 or 6 cm. long: calyx hemispherical, canescent, 8 to 12 mm. long, cleft half-way to the base into remote lanceolate lobes: corolla 3.5 to 4.5 cm. long, bright red, canescent-tomentulose without, the lips subequal: filaments pilose-hispid; anthers 6 or 7 mm. long, glabrous except at the long-hirsute tip. — OAXACA, Cuicatlan, alt. 555 m., Dec. 2, 1895 (*L. C. Smith*, in exsicc. C. Conzatti, no. 105); between Tlacolula and San Dionisio, Chichicapa, Jan. 3, 1896, and bed of the river Tehuantepec, below Totolapam, Yauhtepec, Jan. 4, 1896 (*C. & E. Seler*, nos. 1673, 1669). Related to *L. laxiflora*, HBK., but differing from that in its much larger petioled leaves and its denser white pubescence.

L. Nelsonii. Shrub with hard ligneous branches covered by smooth gray bark; branchlets bearing irregular areas of leaf-scars; young leaf-bearing branchlets smooth or hispidulous: leaves firm, ovate-lanceolate, 4 to 7 cm. long, 1 or 2 cm. wide, mostly long-acuminate, narrowed below to a short petiole, sharply and irregularly serrate, minutely and sparingly hispidulous: peduncles hispidulous, 1.5 to 4 cm. long, few at the tips of the branches: calyx glabrous, hemispherical, with linear-lanceolate lobes 3 or 4 mm. long: corolla red, 2.5 to 3 cm. long, glabrous within and without: filaments glabrous; anthers 7 mm. long, glabrous except at the bearded tip. — JALISCO, oak woods at 1,380 to 1,694 m. alt., near Huachinango, March 4, 1897 (*E. W. Nelson*, no. 4009). A unique species in Mexico.

L. GRUINA, Cav., var. **conferta.** Coarser and generally more branching than the species: racemes densely flowered, not secund, at first short and capitate, later becoming loose and elongated. — DURANGO, abundant by a creek, Dos Cajetes, alt. 2,620 m., Nov., 1896 (*Edw. Palmer*, no. 810): formerly collected by *Gregg* in 1848–49, but without record of locality (no. 392).

Heterotoma Goldmanii. Annual or biennial, freely branching from the base, 5 dm. high; the slender branches minutely hirsute below with short hairs: leaves mostly toward the base of the plant, thin, lanceolate to ovate, irregularly cut and lobed half way to the middle, 2 to 4 cm. long, on slender petioles one half as long as the blade: racemes elongated, slender and flexuous, pedunculate, loosely-flowered, becoming 2 to 4 dm. long; pedicels filiform, spreading, at first 1 cm. long, in fruit becoming 5 cm. long; bracts subulate, the lowest 1 cm. long, the upper much shorter: calyx hemispherical, glabrous, in fruit 2.5 mm. long, hardly equalling the lance-subulate teeth, and with a linear spur 5 mm. long, bearing 2 subulate awns at the tip: corolla blue, 1.5 cm. long, the posterior portion elongated and adnate to the spur of the calyx; tube cleft nearly to the base; the 3 middle lobes of the limb much larger than the lateral ones. — SINALOA, road from Las Flechas to La Rostra, Feb. 22, 1899 (*E. A. Goldman*, no. 324). Nearest related to *H. macrocenteron*, Benth. in Hook. Ic. xii. 68, t. 1177, but with smaller flowers, looser more spreading inflorescence, and different leaves.

H. stenodonta. Perennial from a slender rootstock: stems slender, glabrous, 3 dm. or less high, leafy to the top: leaves ovate-lanceolate, long-acuminate, 1 dm. or less long, 1.5 to 3.5 cm. broad, thin and glabrous, except for the entire cuneate base, sharply and irregularly serrate with erect narrow-deltoid callous-tipped teeth: racemes terminal or on axillary peduncles, becoming 6 or 7 cm. long; pedicels filiform, ascending, 1 cm. or so long, twice exceeding the subulate minutely toothed bracts: calyx campanulate, the tube in fruit 3 or 3.5 mm. long, about equalling the lanceolate teeth: corolla pale bluish, 8 mm. long, merely gibbous at base: capsule oblong, one-half exceeding the calyx-teeth. — CHIAPAS, Chicharras, alt. 923 to 1,847 m., Feb. 6, 1896 (*E. W. Nelson*, no. 3758).

Brickellia glomerata. Stems closely cinereous with short more or less viscid pubescence, freely branched above: leaves opposite, petioled, ovate to oblong, acute or bluntish, the lower excluding the petioles 8 cm. long, the upper shorter, strongly rugose, scabrous above, tomentulose beneath: heads sessile or subsessile in the upper axils or in terminal leafy-bracted glomerules of from 2 to 5: involucre oblong, 1 to 1.2 cm. long, of about 4 series of oblong or oblong-lanceolate blunt greenish or purplish-brown dark-nerved hardly scarious bracts, the outer and the margins of the inner pilose or arachnoid: achenes linear, 4 mm. long, strongly appressed-pubescent. — GUERRERO, oak woods, higher mountains near Acapulco, Jan., 1895 (*Edw. Palmer*, no. 497): OAXACA,

between Panixtlahuaca and Juquila, alt. 923 m., Feb. 26, 1895 (*E. W. Nelson*, no. 2391); in oak- and pine-woods, San Carlos, Yauhtepec, Jan. 5, 1896, and in mountain-woods between San Carlos and San Bartolo, Jan. 6, 1896 (*C. & E. Seler*, nos. 1765, 1655); previously collected at San Bartolo by *Liebmann* (no. 399), whose specimen has been referred by Dr. Klatt to *B. hebecarpa*, Gray. The present species, however, differs from that as from the other related species in its glomerulate heads and barely scarious involucre.

Xanthocephalum megalocephalum. Perennial from slender running rootstock: stem glabrous, glutinous, 3 or 4 dm. high, bearing 3 or 4 large solitary heads at the tips of long branches: leaves entire, resinous-punctate, the lower spatulate and petioled, about 1 dm. long, the upper lanceolate, sessile and shorter: involucre broad-hemispherical, 10 or 12 mm. high; the outer bracts lanceolate, with herbaceous tips, the inner oblong and blunt, mostly chartaceous: rays oblanceolate, blunt, 2 cm. long: achenes glabrous; pappus a crown of minute pales. — CHIHUAHUA, Mt. Mohinora, Sept. 1, 1898 (*E. W. Nelson*, no. 4890); Sierra Madre near Guachochi, alt. 2,100 m., Sept. 27, 1898 (*E. A. Goldman*, no. 174). Related to *X. Alamani*, Benth. & Hook., but much larger throughout.

Bigelowia Nelsonii. Shrub with rough dark gray bark; branches rigid and ascending, conspicuously glandular-punctate: leaves crowded, linear, submucronate, conspicuously glandular-dotted, 0.5 to 1.5 cm. long: heads solitary, subsessile at tips of short lateral leafy branches: involucre 1 cm. broad, many-flowered, the 3 series of glandular bracts thin, linear-attenuate: achenes long-silky. — CHIHUAHUA, in the Sierra Madre, Sept. 29, 1899 (*E. W. Nelson*, no. 6494). Resembling *B. brachylepis*, Gray, but with much broader heads, and thinner attenuate involucral bracts.

Solidago Pringlei. Stem puberulent or minutely pilose, with few ascending branches, very leafy: leaves linear or elongate-lanceolate, narrowed below to a slender sub-petiolar base, and above to an acuminate tip, 0.5 to 1.3 dm. long, 3 to 7 mm. wide, the midnerve prominent, and two lateral ones sometimes apparent, finely appressed-serrulate or subentire, with ciliate margins, puberulous above, finely pilose beneath: panicles elongate, narrow, 1 to 1.5 dm. long, 2 or 3 cm. broad, secund, the tips slightly recurved: involucre 4 mm. high; bracts glabrous, linear, the outer acutish, the inner blunt: achenes pubescent. — NUEVO LEON, in the Sierra Madre, near Monterey, Aug. 22, 1889 (*C. G. Pringle*, no. 2886). Resembling *S. rupestris*, Raf., but with

more elongated leaves, narrower more secund panicles and much larger heads.

CONYZA LYRATA, HBK., var. pilosa. Branches and younger leaves long-pilose with pale hairs, almost if not quite lacking the viscid character and the glands of the species.— CHIAPAS, on the border of a lake, Tonalá, Paredon, Feb. 8, 1896 (*C. & E. Seler*, no. 1879).

PECTIS LESSINGII, Fernald, Proc. Am. Acad. xxxiii. 67, a species formerly known only from Florida and the West Indies, was collected at Nicoya, Costa Rica, in December, 1899, by A. Tonduz (no. 13791).

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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY
OF HARVARD COLLEGE.

THE SOLUBILITY OF MANGANOUS SULPHATE.

BY THEODORE WILLIAM RICHARDS AND FRANK ROY FRAPRIE.

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THE SOLUBILITY OF MANGANOUS SULPHATE.

By Theodore William Richards and Frank Roy Fraprie.

Presented by T. W. Richards, March 13, 1901. Received March 21, 1901.

The solubility of manganous sulphate has been carefully determined within the past year by F. G. Cottrell,* and the present paper is written to confirm in some measure the results of his work. He was able to disprove by well-considered experiment the less recent work of Linebarger,† who published a singular series of results resting upon faulty reasoning and an erroneous method of experimentation. In a case of this kind, when authorities differ, the truth is more quickly enforced when it is supported, hence the publication of the present paper.

The work to be recorded below was done in the spring of 1898, long before the work of Cottrell. It was part of a still unfinished investigation which has as its object the study of the transition equilibria of potassic manganous sulphate. We hope that circumstances may permit the early publication of the remainder of this work, which has been suspended for a time.‡

It was soon found that a much higher temperature was necessary to drive off the water of crystallization of manganous sulphate than has usually been supposed. Linebarger used only 180°, at which temperature at least one molecule of water remains in the salt if it is surrounded by air with the usual proportion of aqueous vapor. The handbooks name 210° to 240° as the temperature required, and Cottrell, calling attention to Linebarger's error, used 280°. We found that traces of water still remained after heating for half an hour at 350° in an air bath. In this respect the substance reminds one of cupric sulphate.§ The amount thus retained does not much exceed the tenth of a per cent, and the effect upon

* Cottrell, J. phys. ch., 4, 637 (1900).

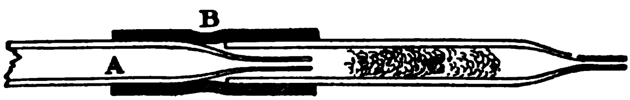
† Linebarger. Am. Chem. Journal, 15, 225 (1893).

‡ A brief statement of the scope and object of this work will be found in Proc. Am. Ass. Adv. Sc., 213 (1898).

§ Richards, Proc. Am. Acad., 26, 240 (1891).

Cottrell's results could not have been serious. On the other hand, a temperature just below redness, perhaps 450°, obtained with a carefully watched naked flame, and applied after long drying at lower temperature, was capable of driving off in five minutes so much of the water that subsequent similar heating for a quarter of an hour showed only an average loss of 0.2 milligram. The product was wholly soluble in water, showing that no decomposition of the sulphate itself had occurred.

The manganous sulphate was purified with great care, and the crystals employed were coarsely powdered. The specimen whose solubility was to be determined was put into a large stout test-tube with a carefully cleaned rubber stopper, and was kept for at least four hours at the desired temperature in an Ostwald thermostat before a sample was taken. The agitation of the mixture was active and continual, being effected by an apparatus similar in principle to that of Schröder.* The motive power was a Henrici hot-air motor. At the close of the appointed time the sample to be analyzed was removed by an effectual filtering pipette, somewhat similar to one which has since been used in van't Hoff's laboratory.† A diagram of the pipette is appended.



FILTERING PIPETTE.

The filtering attachment, filled with cotton wool ("absorbent cotton," C), is temporarily attached to the jet A of a 5-c.c. pipette by means of the rubber tube B.

The cotton was very necessary to filter off the fine powder which appeared during the stirring. In order to avoid change of temperature, the pipette was previously warmed by placing it in a dry test-tube immersed in the thermostat. Only the mouth of the test-tube was allowed to project above the water of the thermostat, and of course every precaution was taken to obtain a fair sample of the solution.

After filling the pipette and quickly removing the rubber filtering-jet attached to it, the clear solution was run into a weighing-bottle and was quickly stoppered and weighed. The known amount of solution was washed into a roomy platinum crucible, when it was cautiously evaporated,

* Schröder, Zeitschr. phys. chem., **11**, 454 (1893); Noyes, ibid., **9**, 606 (1892). For details see Richards and Faber, Am. Chem. Journal, **21**, 168 (1899.)

† Van't Hoff and Meyerhoffer, Z. phys. ch., **27**, 79 (1898).

and the residue was ignited in the fashion already described. In order to make certain that no transition had occurred during the experiment, the crystal-water contained in the solid phase left over after the saturation was always determined. Below are the data thus obtained.

THE SOLUBILITY OF $MnSO_4 . 5H_2O$ AT 25°.

No. of Determination.	Time of Saturation.	Weight of Solution.	Weight of $MnSO_4$.	$MnSO_4$ for 100 gr. Water.
	hours.	grams.	grams.	grams.
1	6	5.0342	1.9849	65.09
2	6	6.3405	2.4947	64.89
3	8	4.4318	1.7470	65.07
4	8	5.2465	2.0656	64.94
			Average	64.99
5	48	3.4514	1.3622	65.20
6	72	3.5349	1.3947	65.17
			Average	65.19

Cottrell found 64.78 as a mean of two closely agreeing determinations, but the time allowed for saturation was only 2.2 hours. The probable reason for his slightly lower result will be discussed below.

The solubility of the tetrahydrate is recorded on the following page.

The solid material taken from the tubes in Determinations 7 to 10 contained as much as 4.3 molecules of water for each $MnSO_4$, but it was nevertheless probably the designated hydrate containing included mother liquor. The greater solubility of the pentahydrate at 30° would certainly involve the solution of any accessible pentahydrate. The salt remaining from determinations 11 and 12 contained 4.03 molecules of water.

The results at 30.15°, giving an average of 66.38, correspond almost exactly with Cottrell's figure 66.43 at 30°; but in this case his time of saturation was increased to an average of three hours, while ours was not much longer. Hence close correspondence was to have been expected, and the figures mutually support one another. The slight difference may be due to a residual trace of water in Cottrell's salt.

On the other hand, at 35° Cottrell used only two hours for saturation, while we used about seven times as much time. Hence the difference between his result, 67.87, and ours, 68.22, may be explained once more by a difference in the time of mixing.

Until recently the cause of this difference would have been ascribed to a possible incomplete saturation in Cottrell's case; and the higher figures, other things being equal, would have been accepted as the more accurate.

THE SOLUBILITY OF $MnSO_4.4H_2O$ AT 30.15° AND 35.0°.

No. of Determination.	Temperature.	Time of Saturation.	Weight of Solution.	Weight of $MnSO_4$.	$MnSO_4$ for 100 gr. Water.
		hours.	grams.	grams.	
7	30.15°	4	4.3125	1.7215	66.44
8	30.15°	4	5.7567	2.2948	66.27
9	30.15°	4	4.5992	1.8339	66.32
10	30.15°	4	5.2822	2.0894	66.48
			Average	. . . . . .	66.38
11	35.0°	13	3.7009	1.5007	68.21
12	35.0°	14.5	2.7854	1.1296	68.22
			Average	. . . . . .	68.22

While this may be true, the recent work of Ostwald* on the solubility of powders and the surface tension of solids has thrown new light on this matter, and it seems quite possible that neither series of results may be perfectly definite. Fine powders have a greater solution-tension than coarse ones, for the same reason that small drops have a greater vapor tension than large ones.

It has often been stated that very long agitation is necessary to secure saturation.† In view of Ostwald's newer work it seems quite possible that continued active agitation introduces an uncertainty even greater than the one which it avoids. The crystals of salt in the ever-moving tube act as mutual millstones, and gradually wear off one another's

* Ostwald, Z. phys. ch., 34, 495 (1900).

† For example, see Ostwald's Physicochem. Measurements, Walker (Macmillan, 1894), p. 176.

corners, with the production of fine powder. This fine powder must continually dissolve, because it is more soluble than the larger aggregations. At first it will simply hasten the speed of attaining saturation; but later, when saturation with respect to the larger particles has been attained, the fine powder will tend to produce a solution supersaturated with respect to those larger particles. The experience of Cottrell and others seems to indicate that supersaturation is harder to obviate than inadequate saturation. Cottrell, for example, found that $MnSO_4.H_2O$ attained a concentration of 57.41 grams in 100 grams of water after two hours of agitation when the salt was added to pure water, while after twice as long a time the supersaturation in another tube had only been reduced from 72.5 to 62.3 grams per hundred. The solubility found after 27 hours, when both methods gave the same result, was 58.32, or 0.91 grams more than the first and 4. grams less than the second figure.

The outcome of the matter seems to be that constant results upon solubility are usually obtained only when the rate of production of the fine powder exactly balances the rate at which the supersaturation is relieved, and that constant results thus reached represent only a compromise. With cautious agitation, it is possible that a solubility very near that of flat crystal surfaces might be obtained; on the other hand, very active agitation, such as we used, must tend to increase this solubility almost to that corresponding to the fine powder which we always observed in our tubes.

Every one will agree with Ostwald in deciding that the solution tension of flat surfaces, rather than that of sharply curved surfaces, is the quantity which should be determined, if possible. This result would be best obtained by keeping the solid as free as possible from agitation, and driving a constant current of the saturating solution over these resting crystals. A dissolving apparatus which has recently been described, if assisted by a small turbine and suitably immersed in a thermostat, would perhaps be the safest apparatus, although complete saturation would require much time.*

It is evident, as Ostwald points out, that most published determinations of solubility, those of Cottrell and our own included, are subject to a small uncertainty, but it is also evident that the work of Cottrell is by far the most complete work upon the solubility of manganous sulphate which has been published, and that it wholly overthrows the erroneous results of Linebarger.

* Richards, Am. Chem. Journal, 20, 189 (1898).

We determined also the solubility of both the dihydrate and the tetrahydrate of the double sulphate of manganese and potassium, and found solutions saturated at 25.0° with both or either hydrate to yield 40.1 grams of anhydrous solid. Hence this temperature must be near the transition temperature of the two hydrates. The detailed publication of these results and many other similar observations must be reserved for a later communication.

In a few words of recapitulation, the present paper may be said to confirm the work of Cottrell and to disprove that of Linebarger, while a measure of doubt is cast upon the usual methods of determining solubility.

CAMBRIDGE, February, 1901.

Proceedings of the American Academy of Arts and Sciences.

Vol. XXXVI. No. 29. — June, 1901.

RECORDS OF MEETINGS.

Nine hundred and seventeenth Meeting.

MAY 9, 1900. — ANNUAL MEETING.

THE Academy met at the Jefferson Physical Laboratory, Cambridge.

VICE-PRESIDENT TROWBRIDGE in the chair.

A quorum not having been present at the adjourned stated meeting of April 11, 1900, on the motion of the Recording Secretary, it was

Voted, That the votes then proposed be now confirmed and approved.

The Corresponding Secretary read letters from Arlo Bates and L. H. Bailey, accepting Fellowship in the Academy. He also read a letter from Seabury C. Mastick, Secretary of the Committee on the Modification of the Federal Legacy Tax, enclosing a new petition intended as a substitute for the one sent out in January and requesting signatures. On the motion of the Recording Secretary, it was

Voted, That the President be authorized to sign this petition on behalf of the Academy.

The Chair announced the death of Frederick Edwin Church, Associate Fellow in Class III., Section 4.

The Annual Report of the Council was read by the Corresponding Secretary.*

The Treasurer presented his annual report, of which the following is an abstract: —

* See Proceedings, XXXV. 628.

General Fund.

Receipts.

Balance from last year		$32.61
Investments	$5,649.80	
Assessments	915.00	
Admission fees	40.00	
Sale of publications	71.23	
Miscellaneous	6.30	6.682.33
		$6,714.94

Expenditures.

General expenses		$2,499.56
Publishing expenses		2,012.73
Library expenses	$1,161.77	
Expenses of moving	596.78	
Furniture	184.60	1,943.15
Balance		259.50
		$6,714.94

Rumford Fund.

Receipts.

Balance from last year		$3,915.10
Investments	$2,566.19	
Sale of publications	10.00	
Refund of appropriation	100.00	
Interest on bank account	71.82	2,748.01
		$6,663.11

Expenditures.

Investigations	$1,215.00	
Medals	327.00	
Library	81.28	
Miscellaneous	10.00	$1,633.28
Income invested during the year and transferred to capital account		3,253.90
Balance		1,775.93
		$6,663.11

Warren Fund.

Receipts.

Balance from last year		$1,149.43
Investments	$365.00	
Interest on bank account	50.27	415.27
		$1,564.70

Expenditures.

Investigations	$500.00	
Accrued interest on bonds purchased . . .	70.13	$570.13
Balance		994.57
		$1,564.70

BUILDING FUND.

Receipts.

Balance from last year		$306.03
Investments	$240.00	
Income	21.55	261.55
		$567.58

Expenditures.

Accrued interest on bonds purchased	$28.06
Balance	539.52
	$567.58

The following reports were also presented: —

REPORT OF THE RUMFORD COMMITTEE.

At the last Annual Meeting of the Academy, the sum of $1000 was placed at the disposition of the Rumford Committee for the furtherance of researches in light and heat.

The Committee has made the following appropriations from this fund:

October 11, 1899, it was voted that an appropriation of $500 be made to Professor Edwin B. Frost of the Yerkes Observatory, to assist in the construction of a spectrograph especially designed for the measurement of stellar velocities in the line of sight.

January 10, 1900, it was voted that an appropriation of five hundred dollars be made to Professor Edward C. Pickering of Harvard College Observatory, for the purpose of carrying out an investigation on the Brightness of Faint Stars by coöperation with certain observatories possessing large telescopes.

Furthermore, on January 10, 1900, the Committee voted to ask the Academy to appropriate one hundred dollars from the income of the Rumford Fund to Professor Theodore W. Richards of Harvard University, for a research on the Transition Point of Crystallized Salts, which request was favorably acted upon by the Academy.

And on April 9, 1900, the Committee voted to ask the Academy to appropriate from the same source the sum of two hundred and fifty

dollars to Mr. Arthur L. Clark of the Worcester Academy in furtherance of a research on the Molecular Properties of Vapors in the Neighborhood of the Critical Point. This recommendation has still to be acted upon.

The attention of the Committee had several times been called to the fact that for a long period of years there had been no way, except by a formal vote of the Academy, in which a person other than a member could purchase a copy of the Life and Works of Count Rumford. Meanwhile occasional applications from reputable persons or libraries had been received. The Committee therefore voted on April 9, 1900, to recommend to the Academy that the Treasurer be authorized to make arrangements for their sale to the public, intending that the whole matter of the manner of sale, price, and other details should be left to his discretion. Such authorization was duly granted by the Academy.

The Committee was furthermore advised that there is no copy of the Life and Works of Count Rumford in the Library of the Academy. It was therefore voted at the meeting of April 9, 1900, to recommend to the Academy that a set be added to the library.

At the same meeting it was voted, that the Committee recommend to the Academy the appropriation of one hundred and fifty dollars from the income of the Rumford Fund for the purchase and binding of the usual periodicals for the current fiscal year, together with the following: Deutsche Zeitschrift für Elektrotechnik, L'Éclairage Électrique, Fortschritte der Elektrotechnik.

It was also voted by the Committee that the Chairman recommend that the usual appropriation of one thousand dollars be made by the Academy for the immediate needs of the Committee in furtherance of research.

I have therefore to present the three last-mentioned recommendations for the consideration of the Academy.

The Committee has considered at much length the subject of an award of the Rumford Premium. Among the various candidates whose claims were discussed, there was one who without dissent was considered in the highest degree worthy of the honor. The numerous researches of Professor Carl Barus in various branches of heat, carried on for many years, have uniformly been characterized by great skill, accuracy, and originality, and these valuable contributions to science are generally recognized as of far-reaching importance.

It was unanimously voted by the Committee, for the first time on January 10, and for the second time on April 9, 1900, to recommend to

the Academy at the Annual Meeting the award of the Rumford Medal to Professor Carl Barus, of Brown University, for his various researches in heat.

In response to the usual request, the Chairman of the Committee has received reports of progress from the following persons to whom grants have been made from the Rumford Fund: Professors H. Crew, E. B. Frost, G. E. Hale, E. H. Hall, F. A. Laws, E. L. Nichols, E. C. Pickering, B. O. Peirce, T. W. Richards, and W. C. Sabine.

These reports in full or in abstract are presented as an appendix to this Report.

CHAS. R. CROSS,
Chairman of the Rumford Committee.

APPENDIX.

REPORTS OF PROGRESS TO THE RUMFORD COMMITTEE.
May, 1900.

PROFESSOR HENRY CREW.

Grants of October 26, 1896, $400, for researches on the electrical, chemical, and thermal effects of the electric arc, and May 3, 1899, $200, for researches on the spectrum of the electric arc.

Referring to an "air-tight arc" which he has constructed, Professor Crew says, "This apparatus is well made, and works in a thoroughly satisfactory manner. With it I have made several series of photographs of the arc spectra of iron and magnesium, in an atmosphere of pure hydrogen. These plates I am now measuring up, and hope to be able to publish the results during the coming summer.

"Contrary to expectations, I do not find the iron spectrum at all simplified by the introduction of hydrogen. For while many lines are blotted out, many new ones are introduced by the hydrogen. No less than sixty-two iron lines, either new or profoundly modified, make their appearance between λ 2753 and λ 4415. The origin of these lines I have not yet succeeded in finding.

"I have spent some time also in trying to produce, in this arc, the hydrogen series discovered by Professor Pickering in the star Z Puppis; but I have not found anything resembling such a series."

PROFESSOR EDWIN B. FROST.

Grant of January 10, 1900, $500, to assist in the construction of a spectrograph, especially designed for the measurement of stellar velocities in the line of sight.

"In reply to your inquiry 'as to the present status of researches now in progress which have received aid from the Rumford Fund,' I would state that three remarkably fine prisms have already been purchased, and the other optical parts have been ordered, for the new spectrograph designed for the determination of stellar velocities in the line of sight, in aid of which research a grant of $500 was made last autumn.

"It is hoped that the spectrograph may be completed and the regular work with the instrument may be begun during the present summer, and I shall therefore expect to be able to announce some results of the investigations for your next annual meeting."

PROFESSOR GEORGE E. HALE.

Grant of November 10, 1897, $400, for the purpose of completing a spectroheliograph.

"The spectroheliograph was first attached to the 40-inch telescope last December. Preliminary tests in the laboratory had shown it to be extremely satisfactory from an optical point of view, at least in so far as the definition and contrast of the photographs of spectra were concerned. As we were without a skilled instrument maker at the observatory for several months last summer and autumn, I had the moving plate holder and second slit constructed by an instrument maker in Chicago. The first tests with the telescope showed the presence of a mechanical defect, which caused the plates to be striped with lines a millimeter apart, the pitch of the screw which drives the plate-carriage. A series of experiments showed that these lines were due in large part, if not altogether, to the absence of suitable end-thrust bearings for the screw, and to the poor construction of the screw, nut, plate-carriage, etc. It was then decided to completely reconstruct this part of the spectroheliograph in our own shop. End-thrust bearings were supplied, together with a new screw, which was carefully ground. As the result of the work the millimeter lines did not appear on the photographs taken after the change had been made. It was found, however, that the plate was still covered with fine lines about one quarter of a millimeter apart. These are shown on the plate which I will send you in a few days. In order to remove these lines a large number of experiments were required, but at last, plates practically free from lines, and even smoother than those obtained with the very satisfactory hydraulic apparatus of the Kenwood spectroheliograph, were secured. The diffi-

culty was due in part to errors in the gears, and in part to the theoretically correct double Hooke's joint, which has now been replaced with a belt and pulleys.

"As may easily be imagined, the curvature of the spectral lines in this spectroheliograph is very marked. If the first slit is straight the second slit must be curved, to fit the K line, and the resulting image of the sun is seriously distorted. By dividing the curvature equally between the two slits, and moving the plate in a direction opposite to that employed with a straight first slit, the distortion can be wholly removed. You will notice that the images on the plate sent you are round.

"As soon as the eclipse work is over I hope to return to the spectroheliograph. The preliminary results are such as to lead me to expect much from the instrument."

PROFESSOR EDWIN H. HALL.

Grant of April 26, 1895, $250, in aid of his investigation on the thermal conductivity of metals.

"I expect to read by title a paper at the next meeting of the Academy. I am using some of the money on a side research carried on by Mr. McElfresh, a graduate student, on the thermo-electric effect of hydrogen occluded in nickel. Said effect seems thus far to be lacking."

PROFESSOR FRANK A. LAWS.

Grant of December 13, 1893, in aid of an investigation on the thermal conductivity of metals.

"In respect to the experiments on Thermal Conductivity I can say that this constant for the cast-iron specimen has been determined, and the result calculated. I have not published the method, for the calibration is not satisfactory to me on account of a very peculiar set of readings which I do not feel justified in rejecting. During the examination period I hope to straighten the matter out."

PROFESSOR EDWARD L. NICHOLS.

Grant of October 19. 1894, $250, in aid of investigations on the radiations from carbon at different temperatures.

"I beg to report that my investigation of the visible radiation from carbon, made in part by the aid received from the Rumford Fund, is nearing completion. Spectrophotometric comparisons of the light from

the two varieties of carbon, black and gray, using as a standard the acetylene flame, have been made up to temperatures above 1600°. I am at present struggling with the more difficult range between 1600° and the melting point of platinum. The determination of the higher temperatures offers considerable difficulty as yet, but there are indications which make it seem worth while to carry the investigation to as high a point as possible. The research involves three subordinate investigations, one of which, on the temperatures of the acetylene flame itself, is completed. This I have made the subject of a paper read before the Physical Society. It is likewise printed in the April number of the Physical Review. In my report to the American Academy, I shall incorporate the results of these measurements in connection with the main subject. Of the other two subordinate researches, the study of the thermo elements employed is nearly completed, and a determination of the distribution of energy in the spectrum of the acetylene flame by means of the Nichols radiometer is in progress. The latter is being carried on by one of my assistants, Mr. G. W. Stewart, and we hope as a result of his measurements to obtain a study of the absolute values, by means of which spectrophotometric measurements for different wave lengths can be brought into known relations to each other.

"The work for which the grant was made from the Rumford Fund has required a much longer time than I anticipated, but in spite of the numerous difficulties which we have had to overcome, I think the end is now in sight."

PROFESSOR EDWARD C. PICKERING.

Grant of January 10, 1900, $500 for the purpose of carrying out an investigation on the Brightness of Faint Stars, by coöperation with certain observatories possessing large telescopes.

"An appropriation of five hundred dollars ($500) has been made from the Rumford Fund, to be expended under the direction of Professor Pickering, for the purpose of carrying out an investigation on the brightness of faint stars by coöperation with certain observatories possessing large telescopes. This appropriation results from a communication made to the Council of the American Astronomical and Astro-physical Society held in New York last January. It was represented that the most urgent need of astronomy in America was adequate endowment of the great telescopes of the country so that they could be kept actively at work. It was shown that while the two largest telescopes of the country, and of the world, were kept constantly at work, the means for

the reduction and publication of the observations are wholly inadequate; while some of the largest telescopes in the country, representing a plant costing hundreds of thousands of dollars, are nearly idle and therefore useless. Observations of the greatest value can be obtained with these instruments at small expense, and it is hoped that the beginning now made will justify its permanent continuance on a large scale. The problem undertaken is the determination of the light of faint stars, selected as standards. These will furnish points of reference to which other photometric measures may be referred. Five photometers have been constructed in which, by interposing a photographic wedge of shade glass, an artificial star is reduced in brightness until it appears equal to a real star, as seen in a large telescope. Thirty-six regions have been selected in different parts of the sky, in each of which a series of standards is to be measured. Five stars of about the twelfth magnitude, five of the fifteenth, five of the sixteenth, and five of the seventeenth are to be chosen in each of these regions. The faintest stars will be selected and measured with the Yerkes 40-inch and Lick 36-inch telescopes. Those of the sixteenth magnitude will be measured with the 26-inch telescope of the University of Virginia and perhaps the Princeton 23-inch telescope. The stars of the fifteenth magnitude will be measured with the 15-inch Harvard telescope. All of these stars will be compared with the stars of the twelfth magnitude, when absolute magnitudes will be determined with the 12-inch Harvard meridian photometer. Their relative brightness will also be determined more accurately with the Harvard 15-inch telescope. After the work is fairly started it is believed that it can be reduced to a simple routine, by which great results may be attained with a moderate expenditure. By the time this report is presented, it is expected that observations with the Yerkes, Lick, University of Virginia, and Harvard telescopes will be in progress."

PROFESSOR B. O. PEIRCE.

Grant of December 2, 1892, $200, and April 26, 1895, in aid of an investigation on the propagation of heat in certain solid bodies.

Professor Peirce writes that he "published last summer in the Proceedings of the Academy a short paper on the 'Thermal Conductivity of Vulcanite,' giving therein the results of a long series of experiments. This paper in a somewhat extended form appeared in the Philosophical Magazine."

A paper on the specific heats of different marbles is also ready for publication.

PROFESSOR THEODORE W. RICHARDS.

Grants of October 12, 1898, $200, for the construction of a microkinetoscope, the immediate application of which is to be a study of the birth and growth of crystals; and January 10, 1900, $100, for a research on the transition point of crystallized salts.

"I have had the honor of receiving two grants from the Rumford Fund, the accounts of which have not been closed.

"The first was given for the study of crystal growth by instantaneous photography. Upon this research I have already made several reports. Having pushed the photographic study of the growth of crystals in aqueous solutions to the furthest limit which seemed possible without a very much greater expenditure of money, we have turned our attention to the study of the change of the crystalline structure of iron and steel at a red heat. We have been able so to modify our apparatus, with very slight extra expenditure, that such study seems to be possible.

"The second grant of money was for prosecuting a research on new fixed temperatures for thermometric standardization. Of this grant only $27.50 have thus far been spent for materials which have not yet been exhausted. We have succeeded in showing that the transition temperature of sodic chromate is very near 19.88°, but the exact point cannot be fixed until our thermometers have arrived from the Bureau internationale. These new thermometers are to be the property of the College, hence all the remainder of the Rumford grant ($100 — $27.50 = $72.50) will be available for the special purposes of this particular investigation."

PROFESSOR WALLACE C. SABINE.

Grants of January 12, 1898, $400, and March 15, 1899, $200, for researches on ultra-violet radiation.

Professor Sabine states that Mr. Lyman, who is engaged upon the investigation, "will publish a paper on a by-product of the investigation which seems to me very interesting and important. In this paper he proposes to show that among the spectra formed by the Rowland concave gratings there are spectra not accounted for by the ordinary theory of the grating; that such spectra are common, and at times fairly strong and of excellent definition; that these spectra are diffraction spectra of much less dispersion than the ordinary recognized spectra, and that the errors of ruling to which they are due are not local but general to the whole surface of the grating He will also explain an experimental method of sorting out these lines from the regular and calculable spectra.

These false spectra are especially dangerous in series spectra work, giving a somewhat systematic reproduction of strong lines and groups, which in actual vibration frequencies do not exist. There is some evidence that such errors have been committed in the past, and it was in the presence of such errors that the false spectra were here discovered."

Report of the C. M. Warren Committee.

In behalf of the C. M. Warren Committee, I have to report that Professor Mabery, to whom a grant of $500 was voted by the Academy at the last Annual Meeting, has vigorously prosecuted his researches on the Composition of Petroleums. During the year he has published also several papers describing the results of his earlier researches which were aided by previous grants from the Warren Fund.

Professor H. O. Hofman, to whom grants, amounting in all to $230, were made several years ago, has in this year published the results of his work in a memoir entitled "The Temperatures at which Certain Ferrous and Calcic Silicates are formed in Fusion, and the Effect upon these Temperatures of the Presence of Certain Metallic Oxides."

The C. M. Warren Committee recommends that the sum of six hundred dollars ($600) from the income of the Cyrus M. Warren Fund be granted to Professor Charles F. Mabery, of Cleveland, Ohio, for the continuation of his researches on the Chemistry of Petroleums.

F. H. Storer, *Chairman.*

9 May, 1900.

Report of the Committee of Publication.

The Publishing Committee reports that during the past academic year there have been issued three numbers of Vol. XXXIV. and twenty-two numbers of Vol. XXXV. of the Proceedings, aggregating 579 pages, with no plates. One number only has been printed at the charge of the Rumford Fund. The expenditure from the General Fund was $2,012.93, out of an available amount from appropriation and sales of $2,471.23, leaving an unexpended balance of $458.30. The Committee desires for the coming year the same appropriation as for the last, viz., $2,400.

For the Committee,

Samuel H. Scudder, *Chairman.*

Report of the Committee on the Library.

The most important feature of the year was the removal of the Library from the Boston Athenæum building to the third story of the new building of the Massachusetts Historical Society. Although it was expected that these quarters would be ready in April, 1899, it was six months later before they could be occupied. The books, etc., were moved in good order between October 17 and November 7, 1899, thanks to the careful supervision of Dr. Holden, the Assistant Librarian. The opportunity was taken to send to the binder many volumes which had accumulated from previous years. The storage-room in the basement of the new building could not be occupied until April, 1900, and during the first week of that month the publications of the Academy, which had been stored in the basement of the Athenæum, were brought there.

The accessions during the year have been as follows: —

	Vols.	Parts of vols.	Pams.	Maps.	Total.
By gift and exchange	431	1687	328	5	2451
By purchase — Gen'l Fund	25	593			618
By purchase — Rumf. Fund		155			155
Total	456	2435	328	5	3224

The total number compares with 3284 during the previous year.

25 volumes and 593 parts of volumes were bought with the appropriation from the income of the General Fund at an expense of $191.35. 155 parts of volumes were bought with an appropriation from the income of the Rumford Fund for $24.28.

449 volumes were bound at an expense of $504.55, of which $487.00 was charged to the General Fund, and $17.05 to the Rumford Fund.

202 books have been borrowed by twenty-five persons, including eighteen Fellows of the Academy. 155 of these volumes were borrowed between May and October, 1899, and only 47 between November, 1899, and May, 1900. 22 volumes were not returned before May 2nd, in accordance with the rule. It will be noticed that the use of the Library has much diminished during the past six months. During the preceding year 235 volumes were borrowed.

Of the appropriation from the General Fund of $1500, $1161.77 has been spent. This includes $479.74 for incidental expenses of the Assistant Librarian, but does not include about $200 for subscriptions to periodicals not yet paid and about $100 for books now in binders' hands. It

is therefore hoped that the unexpended balance of the
may be reappropriated for next year, making a total

The appropriation from the Rumford Fund was
$41.33 has been spent, $17.05 for binding and $24
but subscriptions to periodicals aggregating about $6
must still be paid for. Therefore it is desired that
appropriation, viz. $78.67, be reappropriated for ne
to the $150 recommended by the Rumford Commi
needed to complete the file of the "Fortschritte de
was voted to purchase, have been ordered.

The cost of moving the Library and belongings, w
pay from the funds of the Academy, was $601.78.

Of the special appropriation of $200 for furni
$184.60 has been spent. This includes $30 for the
writer which has been useful to the Recording Secret
Assistant Librarian.

In conclusion, the need of a new catalogue of th
At present there is only an author-catalogue writte
large cards, and the writing is often nearly illegible. S
demands a modern catalogue of authors and subjects, e
printed on standard cards. The cost of such a catal
but a special appropriation of $200 is asked for, to co

A. LAWRE

Librarian, and C

on the

BOSTON, MAY 9, 1900.

In accordance with the recommendations
above reports, it was

Voted, To award the Rumford Medal to C
various researches in heat.

Voted, That a set of the Life and Works of
be added to the Library of the Academy.

Voted, To appropriate one hundred and fif
from the income of the Rumford Fund for t
binding of the usual periodicals for the cu
together with the following: Deutsche Zeit
trotechnik, L'Éclairage Électrique, and Fortsc

Voted, That the sum of one thousand doll

the income of the Rumford Fund be placed at the disposal of the Rumford Committee to be expended in aid of investigations on light and heat, payments to be made on the order of the Chairman of the Committee.

Voted, That an appropriation of six hundred dollars ($600) from the income of the Warren Fund be granted to Charles F. Mabery of Cleveland, Ohio, for the continuation of his researches on the chemistry of petroleum.

Voted, To appropriate twenty-four hundred dollars ($2400) from the income of the General Fund for the expenses of publication.

Voted, To appropriate eighteen hundred and thirty-eight and $\frac{23}{100}$ dollars ($1838.23) from the income of the General Fund and two hundred and twenty-eight and $\frac{67}{100}$ dollars ($228.67) from the income of the Rumford Fund, in addition to the amount recommended by the Rumford Committee, for library expenses.

Voted, to appropriate two hundred dollars ($200) toward making a new catalogue of the Library.

On the recommendation of the Committee of Finance, it was

Voted, To appropriate two thousand dollars ($2000) from the income of the General Fund for general expenses.

Voted, That the assessment for the ensuing year be five dollars.

On the motion of S. H. Scudder, it was

Voted, To meet on adjournment on the second Wednesday in June.

The annual election resulted in the choice of the following officers and committees: —

ALEXANDER AGASSIZ, *President.*
JOHN TROWBRIDGE, *Vice-President for Class I.*
ALPHEUS HYATT, *Vice-President for Class II.*
AUGUSTUS LOWELL, *Vice-President for Class III.*
WILLIAM M. DAVIS, *Corresponding Secretary.*
WILLIAM WATSON, *Recording Secretary.*
FRANCIS BLAKE, *Treasurer.*
A. LAWRENCE ROTCH, *Librarian.*

Councillors.

Henry Taber, Theodore W. Richards, Harry M. Goodwin,	of Class I.
William T. Councilman, John E. Wolff, George H. Parker,	of Class II.
James B. Ames, William Everett, A. Lawrence Lowell,	of Class III.

Member of the Committee of Finance.

Augustus Lowell.

Rumford Committee.

Erasmus D. Leavitt, Amos E. Dolbear,
Edward C. Pickering, Arthur G. Webster,
Charles R. Cross, Theodore W. Richards,
Thomas C. Mendenhall.

C. M. Warren Committee.

Charles L. Jackson, Leonard P. Kinnicutt,
Samuel Cabot, Arthur M. Comey,
Henry B. Hill, Robert H. Richards,
Henry P. Talbot.

The following gentlemen were elected members of the Academy: —

Jay Backus Woodworth, of Cambridge, as Resident Fellow in Class II., Section 1 (Geology, Mineralogy, and Physics of the Globe.)

Merritt Lyndon Fernald, of Cambridge, as Resident Fellow in Class II., Section 2 (Botany).

William Ernest Castle, of Cambridge, as Resident Fellow in Class II., Section 3 (Zoölogy and Physiology).

George Mercer Dawson, of Ottawa, as Associate Fellow in Class II., Section 1 (Geology, Mineralogy, and Physics of the Globe), in place of the late Sir John William Dawson.

Melville Weston Fuller, of Washington, as Associate Fellow in Class III., Section 1 (Philosophy and Jurisprudence).

Rufus Byam Richardson, of Athens, as Associate Fellow in Class III., Section 2 (Philology and Archaeology).

Thomas Day Seymour, of New Haven, as Associate Fellow in Class III., Section 2.

Henry Morse Stephens, of Ithaca, as Associate Fellow in Class III., Section 3 (Political Economy and History).

William Cawthorne Unwin, of London, as Foreign Honorary member in Class I., Section 4 (Technology and Engineering).

Sir Archibald Geikie, of London, as Foreign Honorary Member in Class II., Section 1 (Geology, Mineralogy, and Physics of the Globe), in place of the late Carl Friedrich Rammelsberg.

Sir John Murray, of Edinburgh, as Foreign Honorary Member in Class II., Section 1, in place of the late Alfred Louis Olivier Legrand Des Cloizeaux.

Arthur G. Webster called attention to the bill before the House of Representatives for the establishment of a National Standardizing Bureau, and on his motion, it was

Voted, That the Academy approves this project.

On the motion of W. M. Davis, it was

Voted, That the committee appointed at the meeting of April 11, 1900, to consider the propriety of amending the first chapter of the Statutes be instructed to correct certain clerical errors in the Statutes.

Clarence J. Blake made some remarks on the scientific researches of his father, the late John H. Blake, which he intended to describe more fully in a forthcoming biographical notice.

John Trowbridge described some results obtained with a storage battery of twenty thousand cells and exhibited the battery in operation.

Experiments on the passage of powerful discharges through minute orifices were described, and proofs of the oscillatory nature of sparks six feet long were given. Since these sparks closely represent the main features of lightning, it is probable that most lightning discharges are also oscillatory. The battery with the aid of large condensers furnishes

powerful quantity discharges which are more interesting from a scientific point of view than discharges of high electromotive force; for a new field appears to be opened in spectrum analysis. Photographs of the spectra of gases can be obtained with one or two discharges with a narrow slit.

Perhaps the most interesting results obtained with the battery were from the methods of exciting the X-rays. Photographs of the usual subjects treated by these rays can be taken, and they exhibit great contrasts; moreover, there are traces of ligaments and muscles as well as bones. The members of the Academy visited the battery room and saw a hydrogen tube excited by the discharge from three hundred Leyden jars, and the lighting of an X-ray tube.

The following papers were presented by title: —

Paleontological Notes V. A New Fossil Crab from the Miocene Greensand Bed of Gay Head, Martha's Vineyard, with Remarks on the Phylogeny of the Genus Cancer. By Alpheus S. Packard.

On the Thermal Diffusivities of Different Kinds of Marble. By B. O. Peirce and R. W. Willson.

Paleontological Notes VI. On Supposed Merostomatous and Other Paleozoic Arthropod Trails, with Notes on those of Limulus. By Alpheus S. Packard.

On the Continuity of Groups generated by Infinitesimal Transformations. By S. E. Slocum. Presented by Henry Taber.

On the Thermal and the Electrical Conductivity of Soft Iron. By Edwin H. Hall.

An Apparatus for Recording Alternating Current Waves. By Frank A. Laws.

The Dinitro Compounds of Paradibrombenzol. By C. Loring Jackson and D. F. Calhane.

On Certain Derivatives of Orthobenzoquinone. By C. Loring Jackson and Waldemar Koch.

Geometry on Ruled Quartic Surfaces. By F. B. Williams. Presented by W. E. Story.

On the Action of Sodic Sulphite on Tribromdinitrobenzol and Tribromtrinitrobenzol. By C. Loring Jackson and Richard B. Earle.

Nine hundred and eighteenth meeting.

JUNE 13, 1900. — ADJOURNED ANNUAL MEETING.

A quorum was not present and the Academy was not called to order.

Nine hundred and eighteenth Meeting.

OCTOBER 10, 1900. — STATED MEETING.

The CORRESPONDING SECRETARY in the chair.

The following letter was read: —

843 EXCHANGE BUILDING, BOSTON,
September 5, 1900.

FRANCIS BLAKE, ESQ.,
Treasurer of the American Academy of Arts and Sciences.

DEAR SIR, — By a letter enclosed in his will, my Father, Mr. Augustus Lowell, requested his sons to pay "to the American Academy of Arts and Sciences $10,000." It gives me great pleasure to enclose to you, in accordance with this request, a check for the amount named.

Very truly yours,
A. LAWRENCE LOWELL.

The Corresponding Secretary also read letters from W. E. Castle, M. L. Fernald, Jeremiah Smith, and J. B. Woodworth, accepting Fellowship; from George M. Dawson, M. W. Fuller, T. D. Seymour, and H. M. Stephens, accepting Associate Fellowship; and from Sir Archibald Geikie, F. Kohlrausch, Sir John Murray, and W. C. Unwin, acknowledging election as Foreign Honorary Members.

Announcement was received of the death of D. T. Day, formerly President of the Buffalo Society of Natural Sciences.

The following deaths were announced: —

Augustus Lowell, Vice-President for Class III.; John Elbridge Hudson, of Class III., Section 1., Sylvester R. Koehler, of Class III., Section 4, Resident Fellows; James Edward Keeler, of Class I., Section 1, Jacob Mandes DaCosta, and Alfred Stillé, of Class II., Section 4, William Mitchell, of Class III., Section 1, Associate Fellows; Willy Kühne, of Class II., Section 4, Charles Russell, Baron Russell of Killowen, and Henry Sidgwick, of Class III., Section 1, Foreign Honorary Members.

The Chair appointed the following standing committees: —

Committee of Publication.

SAMUEL H. SCUDDER, SETH C. CHANDLER,
CRAWFORD H. TOY.

Committee on the Library.

A. LAWRENCE ROTCH, HENRY W. HAYNES,
SAMUEL HENSHAW.

Auditing Committee.

HENRY G. DENNY, WILLIAM L. RICHARDSON.

The Chair appointed from the next retiring Councillors

THEODORE W. RICHARDS, of Class I.,
WILLIAM T. COUNCILMAN, of Class II.,
JAMES B. AMES, of Class III.,

a committee to nominate candidates for the offiees made vacant by the death of Augustus Lowell.

Thomas Messenger Drown, of South Bethlehem, was elected an Associate Fellow in Class I., Section 3 (Chemistry).

J. H. Wright gave an account of "Recent Excavations in Crete," by Miss Helen S. Boyd, of the American School at Athens.

Barrett Wendell read an essay on the "Literary History of America."

W. M. Davis presented some "Geographical Notes on Brittany and Devonshire."

The following paper was presented by title by W. C. Sabine: —

False spectra from the Rowland Concave Grating. By Theodore Lyman.

Nine hundred and nineteenth Meeting.

NOVEMBER 14, 1900.

The CORRESPONDING SECRETARY in the chair.

The Corresponding Secretary read a letter from the American Chemical Society transmitting resolutions relative to the establishment of a National Standards Bureau in connection

with the United States Office of Standard Weights and Measures and requesting coöperation in its efforts to secure the establishment of such bureau.

On the motion of Arthur G. Webster, it was

Voted, That this matter be referred to a committee to be appointed by the Chair.

The committee was constituted as follows: —

JAMES M. CRAFTS, *Chairman*,
ARTHUR G. WEBSTER,
THEODORE W. RICHARDS,
EDWIN H. HALL.

On the motion of Barrett Wendell, the following resolution was adopted: —

Whereas, The Academy has received the sum of ten thousand dollars paid by the sons of the late Augustus Lowell at the request of their father, therefore be it

Resolved, That the Academy accepts this gift with grateful appreciation of the generosity of its late honored Vice-President, and that the Corresponding Secretary notify this action to Mr. Lowell's sons.

The following papers were presented by title: —

On the Composition of California Petroleum. By Charles F. Mabery and Edward J. Hudson.

On the Chlorine Derivatives of the Hydrocarbons in California Petroleum. By Charles F. Mabery and Otto J. Sieplein.

On the Composition of Japanese Petroleum. By Charles F. Mabery and Shinichi Takano.

James Ford Rhodes read an account of "Sherman's March to the Sea," of which the following is an abstract: —

After the capture of Atlanta, the question in Sherman's mind was how he should still further proceed on the offensive. Hood gave him trouble by severing his communications, but he could not be brought to a battle, nor could he be caught in a pursuit. Sherman resolved to leave Tennessee in the care of Thomas and march through Georgia to the sea. He severed his communications with the North, November 12, 1864, and from that day to December 14 no direct intelligence from him

reached the North. There was little fighting, but the supply of 62,000 troops in the enemy's country called for foresight and system on the part of the general; to prevent the host from degenerating into a lawless mob required the enforcement of discipline by the general and his officers. The army foraged liberally on the country in an orderly manner. While there were some abuses, some wanton destruction of property, and some pillage, there were no cases of murder or rape. On the whole the army behaved as well as could have been expected. Sherman estimated the damage done to the State of Georgia at $100,000,000. On the night of December 20, 1864, the Confederates evacuated Savannah, Sherman took possession of the city, and sent his celebrated Christmas-gift despatch to President Lincoln.

H. Helm Clayton read a paper entitled: "The Eclipse Cyclone and the Diurnal Cyclone: Results of Meteorological Observations during the Solar Eclipse of May 28, 1900."

Nine hundred and twentieth Meeting.

DECEMBER 12, 1900.

The Academy met at the house of William W. Jacques.

The PRESIDENT in the chair.

The death of Thomas Gaffield, Resident Fellow in Class I., Section 3, was announced.

On the motion of the Corresponding Secretary, it was

Voted, That a committee be appointed to make revision of certain passages in the Statutes and report thereon to the Academy.

. This committee was constituted as follows: —

The PRESIDENT,
The CORRESPONDING SECRETARY,
C. LORING JACKSON.

Wallace C. Sabine spoke on "The Influence of Architecture on Melody and the Development of the Musical Scale."

John E. Wolff described the celebration of the two-hundredth anniversary of the foundation of the Royal Academy of Sciences, at Berlin, on the 19th and 20th of March last, which John W. White and himself attended as delegates from the American Academy.

William Everett gave an account of the life and works of the late Henry Sidgwick, referring particularly to his eminent ability and estimable character.

The following paper was read by title: —

"Symmetrical Triiodbenzol." By C. Loring Jackson and G. E. Behr.

Nine hundred and twenty-first Meeting.

JANUARY 9, 1901. — STATED MEETING.

VICE-PRESIDENT HYATT in the chair.

On the motion of C. L. Jackson, it was

Voted, To defer action on the proposed amendments of the Statutes.

Voted, That the Academy send a message of congratulation to Vladimir Markovnikoff, of Moscow, on the occasion of the 40th anniversary of his work on chemistry.

The vacancies occasioned by the death of Augustus Lowell were filled by the election of

JAMES B. THAYER, *Vice-President for Class III.*

ELIOT C. CLARKE, *Member of the Committee of Finance.*

Denman W. Ross read a paper entitled, "Design as a Science."

S. C. Chandler gave an account of his "New Discovery concerning the Motion of the Earth's Pole."

The following papers were presented by title: —

"Suggestion concerning the Nomenclature of Heat Capacity." By T. W. Richards.

"A Study of Growing Crystals by Instantaneous Photomicrography." By T. W. Richards and E. H. Archibald.

Nine hundred and twenty-second Meeting.

FEBRUARY 13, 1901.

The CORRESPONDING SECRETARY in the chair.

The Chair announced the death of Charles Hermite, Foreign Honorary Member in Class I., Section 1.

An invitation to the Ninth Jubilee Celebration of the University of Glasgow was read. On the motion of the Recording Secretary, it was

Voted, That the Academy send delegates to this celebration.

A circular inviting attendance at the Fifth International Congress of Physiologists was read; also, a letter from James B. Thayer, acknowledging his election as Vice-President for Class III.

The following paper was read by title: —

"A Study of Variation in the Fiddler Crab (Gelasimus pugilator Latr.)" By Robert M. Yerkes. A Contribution from the Zoölogical Laboratory of the Museum of Comparative Zoölogy at Harvard College. Presented by E. L. Mark.

Nine hundred and twenty-third Meeting.

MARCH 13, 1901. — STATED MEETING.

VICE-PRESIDENT HYATT in the chair.

The following deaths were announced: —

Charles Carroll Everett, Resident Fellow in Class III., Section 1.

George Mercer Dawson, Associate Fellow in Class II., Section 1.

The following gentlemen were elected members of the Academy: —

Alexander Wilmer Duff, of Worcester, as Resident Fellow in Class I., Section 2 (Physics).

Theodore Lyman, of Brookline, as Resident Fellow in Class I., Section 2.

Lewis Jerome Johnson, of Cambridge, as Resident Fellow in Class I., Section 4 (Technology and Engineering).

Henry Lloyd Smyth, of Cambridge, as Resident Fellow in Class I., Section 4.

Frank Shipley Collins, of Malden, as Resident Fellow in Class II., Section 2 (Botany).

Ephraim Emerton, of Cambridge, as Resident Fellow in Class III., Section 3 (Political Economy and History).

Frank William Taussig, of Cambridge, as Resident Fellow in Class III., Section 3.

Eliakim Hastings Moore, of Chicago, as Associate Fellow in Class I., Section 1 (Mathematics and Astronomy).

George Ellery Hale, of Williams Bay, as Associate Fellow in Class I., Section 2 (Physics).

Edward Leamington Nichols, of Ithaca, as Associate Fellow in Class I., Section 2, in place of the late William Augustus Rogers.

Cyrus Guernsey Pringle, of Charlotte, Vermont, as Associate Fellow in Class II., Section 2 (Botany), in place of the late George Clinton Swallow.

Franklin Paine Mall, of Baltimore, as Associate Fellow in Class II., Section 3 (Zoölogy and Physiology), in place of the late Alfred Stillé.

Henry Fairfield Osborn, of New York, as Associate Fellow in Class II., Section 3, in place of the late Othniel Charles Marsh.

Charles Otis Whitman, of Chicago, as Associate Fellow in Class II., Section 3.

William Stewart Halsted, of Baltimore, as Associate Fellow in Class II., Section 4 (Medicine and Surgery), in place of the late William Alexander Hammond.

William Williams Keen, of Philadelphia, as Associate Fellow in Class II., Section 4, in place of the late Jacob Mandes Da-Costa.

Jules Henri Poincaré, of Paris, as Foreign Honorary Member in Class I., Section 1 (Mathematics and Astronomy), in place of the late Francesco Brioschi.

Heinrich Müller-Breslau, of Berlin, as Foreign Honorary Member in Class I., Section 4 (Technology and Engineering).

Hugo Kronecker, of Bern, as Foreign Honorary Member in Class II., Section 3 (Zoölogy and Physiology), in place of the late Willy Kühne.

Sir Thomas Lauder Brunton, of London, as Foreign Honorary Member in Class II., Section 4 (Medicine and Surgery), in place of the late Sir James Paget, Bart.

Robert Koch, of Berlin, as Foreign Honorary Member in Class II., Section 4, in place of the late Louis Pasteur.

Albert Venn Dicey, of Oxford, as Foreign Honorary Member in Class III., Section 1 (Philosophy and Jurisprudence).

William Edward Hearn, of Melbourne, as Foreign Honorary

Member in Class III., Section 1, in place
Russell, Baron Russell of Killowen.

Henry Jackson, of Cambridge, as Foreign
in Class III., Section 2 (Philology and Arc
of the late Henry Sidgwick.

Edmondo de Amicis, of Florence, as Fore
ber in Class III., Section 4 (Literature and
place of the late John Ruskin.

On the motion of the Corresponding Secre

Voted, To meet, on adjournment, on the 1

B. L. Robinson gave an account of " Rece
General Classification of the Flowering Plan

R. T. Jackson spoke on " Resorption as a

The following papers were presented by ti

The Occlusion of Magnesic Oxalate by C
the Solubility of Calcic Oxalate. By Theo
Charles F. McCaffrey, and Harold Bisbee.

Contributions from the Cryptogamic Lab
University, XLVI. Preliminary Diagnoses
Laboulbeniaceae, III. By Roland Thaxter.

The Development and Function of Reiss
Cellular Connections. By Porter E. Sargent
L. Mark.

The Solubility of Manganous Sulphate.
Richards and F. R. Fraprie.

Contributions from the Gray Herbarium
versity. New Series, No. XX. I. Synoj
Melampodium. II. Synopsis of the genus
Species and Newly Noted Synonymy amo
phytes of Mexico and Central America. By

Contributions from the Gray Herbarium o
sity. New Series, No. XXI. By M. L. Fe
Spermatophytes from Mexico and Central A

doubtedly, have been distinguished, but he had a very great and unusual capacity for business, for shaping large affairs and for influencing men, a faculty that would have largely missed its opportunity in the quiet life of a college officer.

He entered the office of Messrs. Chandler, Shattuck and Thayer, as a student, in Boston, in 1865 or 1866. Admitted to the Suffolk Bar in October, 1866, he soon became managing clerk in the office of the firm just mentioned on terms which indicated a high appreciation of his ability; and in February, 1870, on the retirement from the firm of Mr. George O. Shattuck, he became its junior member. Here he continued, during some changes in the firm, until its dissolution in 1878. In the interval between this and the year 1880, when that connection with the telephone business began which was to last for the remaining twenty years of his life, he practised law alone, and added some editorial work upon the tenth volume of the United States Digest. That was a task which it was quite possible to carry through in a seemingly respectable and yet entirely perfunctory fashion. But Mr. Hudson took it up as he took up everything, and planned a volume of distinguished merit. On entering the service of the telephone company he had to leave the completion of the book to another; but he had begun by making a new analysis and classification of the titles of the law employed in the Digest, — one which was so much valued that it forms to-day the model of a recent great undertaking by a Western publishing house, known as the Century Digest, now in general use among lawyers.

Mr. Hudson was thus an active member of the bar for fourteen years. His preference was for office work; very seldom could he be induced to try a case, or to argue a point of law before a court. During the nine years that we were connected with the same firm, before I went to the Law School, in 1874, I can speak of his work from an intimate knowledge of it. He had the oversight of our accounts, and took charge of a great part of the office work, such as the drawing of contracts and wills, and the preparation of pleadings and court papers. In all this, his work was admirably well done. The character of it, at a little later period, attracted the attention of the Chief Justice of the Supreme Court, who sent for him and expressed a wish that he would take the place of Clerk of that court. I recall also the great satisfaction expressed by a client, a very able business man in the China trade, who had had occasion to consult him about some tangled affairs. "I have not seen," he said, "such a head for complicated accounts since my early experience with John M. Forbes."

As I have said, there was another department of work in which it was practically impossible to interest Hudson, that is to say, work in court. You could hardly drive him to take hold of that. He took no pleasure in it and showed little capacity for it. He was always a shy person, little inclined to put himself forward, and absolutely unwilling to appear in public, if he could avoid it; and for that reason the breadth and versatility of his extraordinary powers were sometimes overlooked. Indeed many of those who knew him well and best appreciated his remarkable qualities were surprised at the developments of later years.

Early in 1880, Colonel William H. Forbes, the President of what was soon to become the American Bell Telephone Company, who had known Mr. Hudson in college and also as a lawyer, invited him to become the Solicitor of the Company. The invitation was accepted, and Hudson entered at once upon his new duties. Five years later he was asked to become the General Manager. To accept such a place as that was a serious step. So far he had not left the law, but this new proposition would plunge him into a career of business, and business of a very engrossing sort. He came to talk it over with me; and I had many misgivings. He knew, the Company knew, all his friends knew, what he could do in the law. But this was a new venture. What if all this tremendous, novel, swiftly developing business should not suit him, or should prove too much for him? Was he sure that he could handle it?

I was greatly impressed by his answer. Oh, yes, indeed; as to that he had no doubt whatever; he could handle it well enough. As Solicitor he had got a good insight into the nature of it all, and he had no fears on that head. This confidence in his own powers of dealing with the men and the affairs of so great a concern, a confidence fully justified by the event, opened my eyes to a new side of Hudson's capacity. He took the office, without relinquishing the place of Solicitor, filled it to the entire approval of the Company, added to it the next year that of Vice-President, and in 1887 that of President of the American Telephone and Telegraph Company, then known as The Long Distance Company, and two years later became President also of the main organization, the American Bell Telephone Company. These last two offices he held with great success and distinction up to the time of his death; for the final steps in the absorption of the last named company in the first were not then, and I believe are not yet, completed.

Of the ability which Mr. Hudson showed in guiding and shaping the development of this new and complex industry of the telephone, others

who were associated with him have already spoken. Mr. Francis Blake, one of the directors of the Telephone Company, has said that while Mr. Hudson was Manager and President the number of miles of telephone increased more than tenfold, to over a million miles in 1899, and the number of exchange connections more than sixfold, reaching nearly seventeen hundred millions in the same year; and he adds: "Moreover, during this period there was conceived and developed a system of long-distance service which brought more than half the population of the United States within the limits of telephonic speech. These statistics," he adds, "emphasize the broad statement that the growth of Mr. Hudson's business capacity not only kept pace with, but kept in advance of the ever increasing needs of the companies under his control." *

Added to great intellectual capacity, to a remarkable strength, grasp, and tenacity of mind, Mr. Hudson had another source of power, — his sound moral quality. He made no parade of his integrity, but he was thoroughly honest and honorable, and all who dealt with him saw it. In one of the Company's great law-suits an antagonist thought fit to charge it with indirection in a particular matter. The counsel of the Company, the late William G. Russell, met the charge with a statement by Mr. Hudson. "And I need not say to the court," he added, "that on a question of fact within his knowledge, the word of John E. Hudson imports absolute verity." To a specific reliance upon these personal qualities of the President of the Telephone Company, upon his great intellectual gifts, his forecasting and shaping power, his sound judgment, cautious and yet bold in advancing to meet the great emergencies which he foresaw, upon his absolute integrity and his power over men, in a word, to personal confidence in him, may be traced the investment of millions of dollars in that great corporation.

Undoubtedly Mr. Hudson sacrificed his life to the enormous and ever-growing requirements of the office which he held. It was his habit to rest by going abroad for a month or two in the summer, and to pass the remainder of that season at the seashore within easy reach of his office. It is said, and probably with truth, that he lacked somewhat in one of the qualities of a great administrator, namely, in the power to turn over work to subordinates. He could not bear to see work imperfectly done, when he himself could do it so thoroughly well. His friends had long urged him to withdraw from these heavy cares, and a few years ago he had

* Memoir by Francis Blake; Proceedings of the American Antiquarian Society, October 24, 1900.

well-nigh done it. But he was persuaded to remain, arranging at that time to withdraw in the year 1900. Doubtless, like all strong men, he enjoyed the exercise of his strength. Moreover, the development of the business and increasing complications seemed to demand his personal attention just a little longer, — and so the end came as it did. He seemed, for the most part, to bear it all easily enough, but the strain was immense, incessant, increasing; and before he knew, it was too late.

A word or two more should be said as to Mr. Hudson's mental habits, and his methods of working; and a word or two also as to the personal qualities that made him much beloved.

At home Mr Hudson used to have by the side of his plate, as he sat at table, a pencil and paper, for he knew the worth of a memorandum taken at the moment. In his business he was in the habit of causing to be taken and preserved such memoranda of all that took place at each stage of any particular affair. This full record, perfectly arranged and indexed, was of the utmost service to him in handling his great business. He had only to turn to his books to find a record of everything. Often, indeed, he had no need to turn to his books, unless to convince his interlocutor; for he had an extraordinary capacity of remembering facts, of *visualizing* them, and holding them all mapped and co-ordinated in his mind.

In his private studies he was apt to begin by preparing a chart of the subject, with names and dates and the order and place of leading facts and events, all set forth with extraordinary neatness, open to inspection, and speaking volumes to a glance of the eye. These things, thus quickly visible, passed over into his mind and stood there fixed permanently in a rational order. It was so with places. London and Paris and all their streets *he saw*. He had explored the maps so that he hardly needed them longer. His mind held the maps.

This faculty gave an extraordinary interest to his conversation. Last summer I passed several days with him at his house, and he, later, a week with me at mine. He had been reading Plutarch, and everything about him that he could lay hands on. He was trying to place him and his thought in their true relation to the men and the ideas of the time just past and just to come. He had been reading also of Alexander, and reading with equal ease in the Greek and Latin authors as in those in our own tongue. It was a pleasure of the highest sort to listen to his talk. The precision and extent of his knowledge, the way in which it lay in his mind, co-ordinated with whatever related things threw light

upon it, these and the breadth and illuminating good sense of his own reflections were equally instructive and delightful. Alexander and Plutarch stood out before you in their true place in history, and in their true relations to the men, the dates, and the events of their time.

No one could see Hudson without guessing at the strength and force of his character; and no one who knew him well could fail to see that under his gentle demeanor there lay qualities of energy and passion that were not to be trifled with when once they were aroused. But he was an affectionate and charming friend, and one that women and little children and those who were dependent upon him loved.

Mr. Hudson married in 1871 Miss Eunice Wells Healey, of Hampton Falls, New Hampshire, who survives him, to bear a most heavy loss. He left no children. One sister also survives him, the wife of Samuel J. Hollis of Lynn.

He went little into society and but little to the larger clubs.* He was happiest at home, and there he gave himself up to the refined and simple pleasures in which he always had his chief enjoyment. He had a large library, of great range and variety, to which he was forever adding. Most of all he seemed to like, at the end of the day, to sit down among his books and explore his old friends the Greek and Roman classics, — reading them, as he did, with entire ease in the original. When it came to the matter of his real tastes and likings, as his associate Mr. Leverett has happily said, " He was, above all, a scholar, fond of his home."

James B. Thayer.

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* Mr. Hudson was a member of many societies and clubs. In the Memoir for the Historic Genealogical Society, already quoted, Mr. Leverett says: "Mr. Hudson was at the time of his death a vice-president of this Society. He was also a fellow of the American Academy of Arts and Sciences, a member of the Corporation of the Massachusetts Institute of Technology, a member of the American Antiquarian Society, the American Association for the Advancement of Science, the British Association for the Advancement of Science, American Geographical Society, National Geographic Society, the Colonial Society of Massachusetts, the American Institute of Electrical Engineers, the Virginia Historical Society, the Association for the Preservation of Virginia Antiquities, the Bostonian Society, Selden Society, Hakluyt Society, Lynn Historical Society, the Bar Association of the City of Boston, and also of the Algonquin, Boston Art, Exchange, National Arts, St. Botolph, Union, University, and other social clubs." It may be added that he took much pleasure in one or two social clubs made up of college friends or contemporaries.

JOHN HARRISON BLAKE.

In reviewing the printed matter, letters, completed manuscripts, and note-books which furnish the material for a personal memoir of my father, I have been impressed by the paucity of record of the achievements of an active life extending over the greater part of a century.

The reason for this is to be found in the character of the life itself, looking rather to accomplishment than to recognition, and seeking to express the sense of an obligation for the privilege of living by doing the work at hand simply and well.

Of published papers there are but few, — the Transactions of this Academy, of which he was elected a member May 30, 1843, contain none, other journals in the library of the Academy but five, and the records of the Boston Society of Civil Engineers, of which he was one of the founders and its first Secretary, an equally small number.

Of letters, especially family letters, there are many, all clearly written, containing information as to his travels and treating of the subjects in the study of which he was most interested.

Of the manuscripts, the majority, in the form of essays, were written after his retirement from active life with the evident purpose of continuing a companionship which has, to his son, the value both of a precious memory and a continued inspiration; the persistency with which this purpose was pursued, under conditions of failing strength and sight, is shown especially in one of them, begun in ink, continued in black and then in blue pencil when the blue mark alone was visible to him, and concluded by sense of touch.

These essays cover a wide range of scientific subjects and bear witness to an intellectual activity persisting to within the last three years of a life which ended, as gently and as graciously as it had been lived, at the age of ninety years. Through this life there had run one dominant purpose, — that of usefulness; in it there had always been one keen pleasure, — that of scientific research. The note-books, containing many valuable records and memoranda, are the transcripts of a variously active professional life, — one series covers very nearly the whole of the early experimental and constructive history of the manufacture of illuminating gas in this country, another is a record of researches in the chemistry of arts and manufacture, and another is devoted to mining, metallurgy, and civil engineering.

John H. Blake, the youngest son of Thomas and Mary Lowell Barnard Blake, was born December 5, 1808, in the house still standing on

Washington Street, corner of Union Park Street; he died in his home on Marlborough Street, Boston, July 5, 1899, in his ninety-first year. Mr. Blake was educated in private schools and in the English High School, which he entered in 1821 as a member of its first class. Later he became a pupil of the Rev. James Blake Howe, then rector of the West Parish Church in Claremont, N. H., whose daughter, a second cousin, he married on his return from his explorations in South America.

While his studies with Mr. Howe were mainly classical and he was fitted to enter Harvard, his interest in chemistry and in anatomy was such as to lead him to prefer these studies to those of a collegiate course principally literary and mathematical. It was in pursuit of his chosen subjects that, after a period of study in a chemical manufacturing establishment, he became assistant to, and pupil of, Dr. Webster, from whom he received valuable instruction, which enabled him in the year 1827, when only nineteen years of age, to establish, with money advanced by his father, the Norfolk Laboratory, for the manufacture of pure drugs and chemicals. This laboratory was situated in Jamaica Plain near Forest Hills, upon the Dedham Turnpike. One of its products was pure sulphuric ether, and it was in the larger laboratory of later construction that the ether used in the first demonstration of the value of ether anaesthesia was made under Mr. Blake's personal supervision. In addition to the commercial work of the laboratory Mr. Blake carried on a series of investigations into the physiological effects of poisons, the composition of precious stones, and the production of alloys applicable to the mechanic arts. At the end of three years of successful operation the buildings were destroyed by a fire, resulting from the explosion of a carboy of ether, but were immediately rebuilt on a larger scale; a joint stock company was formed, arrangements were made with the Rothschilds for the importation of quicksilver, and with a house in Tuscany controlling what was then the world's principal supply of boric acid; and Mr. Maximilian Isnard, who introduced the manufacture of beet-root sugar into France, became an associate.

At that time but little was known of the sources of supply of nitrate of soda, of which large quantities were used in the works, beyond the names of the small ports on the coast of Peru from which it was shipped.

Ignorance on the subject, the value of the article, and the novelty of entering and exploring an unknown region were sufficient incentives to turn Mr. Blake's thoughts in this direction rather than along the beaten lines of travel in search of the rest and recreation which he needed after eight years of anxious labor. Books gave very little information concern-

ing the country between the Pacific Ocean and the Andes, constituting the extreme southern part of Peru, the western part of Bolivia, and the northern part of Chili, and all the knowledge that could be obtained was that it was, for the most part, uninhabited and uninhabitable, destitute of vegetation, and known as the Desert of Atacama ; it was on the shores of the northern part of this desert that the shipment ports referred to were situated.

The winter of 1835 and 1836 was very cold, New York harbor was frozen over, and it was not until the 10th of February, 1836, nearly a month after the time proposed for her departure, that the ship "Factor," in which Mr. Blake was a passenger, made her way through a channel cut in the ice and sailed for Valparaiso, where she arrived June 9, sailing again on the 9th of July for Arica and Tacna, whence Mr. Blake proceeded by land to Pisaqua and Iquique, arriving at the latter place on the 6th of August. The next three months were devoted to surveys in the province of Tarapaca, and on the 7th of November Mr. Blake left Iquique with a pack train, two Indians, and dogs to make the first recorded exploration of the Desert of Atacama from north to south, arriving at Valparaiso on the 10th of March, having occupied four months and three days in a trying passage over an arid and waterless region, in which all of the animals were lost and the men nearly perished from thirst.

On March 15 Mr. Blake left Valparaiso for Buenos Ayres by Santiago, the pass of Uspalato and Mendoza, crossing the Andes and the Pampas de la Plata, arriving on the 28th of April and making preparations for immediate departure for the United States.*

At this time Rosas, the then Dictator of the Argentine Republic, was engaged in strengthening his position by military activity and the projected subjection of the Indian tribes to the westward. Mr. Blake was detained as consulting engineer on fortifications, and was not released until the autumn of 1837,† when he returned to the United States to find

* The only record of this interesting and perilous journey is to be found in family letters, in the collection of mummies and other objects of archæological value now in the Peabody Museum, Cambridge, and in the description of this collection published from Mr. Blake's notes in the reports of the Museum. The carefully kept notebook, containing not only the daily incidents of travel, but especially the memoranda of geologic observations, of barometric measurements and surveys, was stolen after Mr. Blake's return to this country, and never recovered.

† Information to be derived from a traveller who had just crossed the continent was of value, and Mr. Blake received a courteous note, saying that a house adjoining that of the British Embassy had been placed at his disposal, and requesting him

a condition of general financial disaster, in which the Norfolk Laboratory had shared and which made it impossible to take up the grants for the mining and exportation of nitre secured from the Peruvian government. Under these conditions he accepted the management of the Fernandez copper mines in Santa Clara, Cuba, married, and took up his residence there, where, in addition to the work in hand, he made observations on the character and climate of the country. In 1847 he assisted in the geologic survey of Isle Royale, Lake Superior,* and in 1848 entered into partnership with Franklin Darracott as a civil engineer, to which work he added that of a consulting chemist and geologist. It was his custom to make no charge for consultation to individuals seeking to develop new industries, regarding this as his contribution to the general welfare. Among many to whom he gave valuable advice were Goodyear and Babbitt.

The business of the firm of Blake and Darracott had largely to do with gas engineering and the construction of gas works, and Mr. Blake organized and was at one time president of five gas companies, his executive ability and power of control over men making such work a pleasure. In addition he was interested in iron and gold mining, carrying on the ore beds and blast furnaces and car wheel works at Brandon, Vermont, and organizing and operating the Yahoola River Hydraulic Mining Company, of which he was president, in the Dahlonega belt, Georgia. After the dissolution of the firm of Blake and Darracott he became interested in street railways, building the Middlesex Road and being the President of the Metropolitan Road during the period of the Civil War: subsequently he was President of the Connecticut Arms Manufacturing Company, and organized and was the first President of the Chapman Valve Manufacturing Company.

One of Mr. Blake's latest contributions to manufactures was the so-called antique glass. Wishing to carry out previous experiments on molecular movement in solids at protracted high temperatures, he constructed a crucible furnace in South Boston, and in order to make it pay its expenses manufactured glass upon the basis of his earlier analyses of precious stones, the result being a glass of great brilliancy and vivid color.

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to remain as the guest of the Dictator. The invitation was declined, but was repeated in an equally courteous note brought by a file of soldiers, the note further stating that the Dictator trusted that the invitation would be accepted, as it would pain him to be obliged to provide any narrower accommodation.

* The promontory at the northeasterly extremity of the island is called Blake Point.

The mental activity which had stimulated bodily action beyond the usual term of working years continued to find its expression, even after he had become confined to the limits of his own home, in the manuscripts which contain those products of his mental laboratory impossible of record in busier times; as might be expected they give an insight into the motive power of his life and show the strength of a character which looked forward calmly to bodily dissolution as a part of the process of growth to greater knowledge.

Through the vicissitudes of incessant and protracted work, with the usual meed of disappointment and much of physical pain, Mr. Blake held always the cheerful courage born of a simple faith, which counted life as a primary school and the suffering of his advanced years as a part of its graduating exercises; prominent in my memory of him are his fearlessness, his kindliness, his love of truth, and his earnest desire not to fail in doing his part of the world's work, whatever that might honestly be, and this also, that in fifty-seven years of a dear and close companionship, I cannot recall a single unkind, unjust, or impatient word.

CLARENCE JOHN BLAKE.

CHARLES FRANKLIN DUNBAR.

CHARLES FRANKLIN DUNBAR, Fellow of the American Academy for twenty-eight * years, Professor of Political Economy in Harvard University for nearly thirty years, was born at Abington, Massachusetts, July 28, 1830, and died at Cambridge, Mass., January 29, 1900.

Professor Dunbar's career divides itself into two very different parts; a first, during which he was editor and guiding spirit of the Boston Daily Advertiser; and a second, during which he lived the quiet life of the teacher and scholar.

It was not until he had reached mature manhood that he entered on his newspaper career. After graduating from Harvard College in 1851, he engaged for a short time in business; then, health failing, spent a year in farming; then studied at the Harvard Law School and in the office of the late Justice E. R. Hoar, and was admitted to the Bar in 1858. Meanwhile, contributions from his pen had appeared in the Advertiser; and finally, in 1859, he became permanently associated with

* Elected January 31, 1872.

that newspaper. At first associate editor, he became in 1864 sole responsible editor, and such he remained until he severed his connection with the Advertiser.

The decade during which he was thus in charge of the most influential newspaper in New England was the most trying and perhaps the most important in the country's history. His position as editor brought him into contact with leading men in every sort of career in New England. Both his conduct of the paper, and his association with men, gradually gave him a position of respect and confidence in the community, rarely obtained by those in charge of ephemeral publications. He wrote constantly on a great variety of subjects; on political and military affairs as a matter of course, but with special care and with unusual judgment on the remarkable financial and economic events of the period. His editorials were marked from the outset by the grace and dignity of style which characterized everything that came from his pen. They showed, moreover, the firm and unwavering spirit of the man; never abating by a jot the conviction that in spite of defeat and disaster, in spite of foreign complications and domestic disaffection, the war must be carried on unflinchingly until the supremacy of the Union should be restored. There is not only steadfast faith, but often inspiring eloquence, in the editorial pages of the Advertiser as Professor Dunbar conducted them; and not seldom, after a military failure, his courageous words rang through the community like a bugle blast.

The financial and economic events of this period were of the most extraordinary and varied kind. A huge national debt, a new banking system, an immense and complicated system of taxation, a high protective tariff, an excessive issue of paper money, a wearisome struggle between the advocates of paper money and specie, the turmoil of reconstruction in the South, — such were the phenomena to which the editor of the Advertiser was compelled to give daily attention. His inborn aptitude led him to observe the course of events with keen sagacity, and gave him a fund of experience invaluable for his later career. Few economists have been so fortunate in having been brought into unremitting contact with the actual affairs of life. Few also have been so fortunate in securing contact with men of all classes and all opinions. Daily there came into the office of the editor of the Advertiser persons of every sort, bringing advice, exhortation, information. A characteristic trait of Professor Dunbar's showed itself in these conferences, — a remarkable capacity for silent attention. However certain of his own

ground, he would listen without response to those whose views were different from his own, refrain from stating his objections unless the situation imperatively called for statement, and give his auditor an impression, and a true impression, of respectful and sympathetic interest; and yet in due time would follow the course which his own judgment dictated as wise. The quality of his mind was eminently judicial. He saw all sides of a difficult question so clearly that he sympathized with those who saw perhaps only one side. In the Advertiser office he dealt with business men, statesmen, soldiers, conservatives, radicals, visionaries; learned something from all, dealt courteously with all, gained the respect of all, and yet never failed to maintain his own sound and independent judgment.

The most active and strenuous years of Professor Dunbar's life, between the ages of twenty-nine and thirty-nine, were given to the Advertiser. In his hands its editorship was distinctly a public service; and, cool-headed and sagacious as he was, uninfluenced by any vapid sentimentalism, he so regarded his vocation. But his strength, never very great, was seriously shaken by these ten years of severe application, and in 1869, when the Advertiser changed hands, Professor Dunbar was glad to dispose of his interest and to retire from the paper.

Shortly after, he was offered a professorship of political economy in Harvard University. This was a career he had never looked forward to, and he doubted his own capacity for it. Nevertheless, after some hesitation, he accepted, on condition that he should have time for restoring his strength and adding to his equipment. After two years spent in Europe in study and travel, he entered in 1871 on the duties of the professorship, to which he devoted himself for the rest of his life.

Although thus launched on the career of a scholar and teacher, his abilities were such as to cause him to be enlisted soon in the work of guiding and managing the affairs of the University. On the retirement of the late Professor Gurney, in 1876, he became Dean of the Faculty of Harvard College, and retained that post until 1882. When the present Faculty of Arts and Sciences in Harvard University was organized in 1890, he became its first Dean, and so acted until 1895. In addition, he served frequently on committees, and was in constant intercourse with the President of the University, who relied greatly on his advice. Repeatedly through his academic career, he was called upon to act as judge, as mediator and pacificator, as organizer of new plans, as administrator of new systems. All these duties were discharged with remarkable judgment and success; yet they were felt by him to be

distractions from his chief task as professor in a great institution of learning.

Professor Dunbar's career as editor, and his administrative work in Harvard University, need to be borne in mind when making an estimate of his work as scholar and man of science. To those who knew him well, nothing was more admirable in his career than the solidity of his scholarly attainments, the breadth of his interests, the maturity of his conclusions on his chosen subjects. It might have been expected that one who had been a busy newspaper editor, and who remained to the end keenly interested in current political happenings, should continue to deal largely with questions of the day, and take an active part in current discussion of public issues. Professor Dunbar, however, had too clear a perception of the ideals and duties of a scholar to give himself to newspaper and periodical writing. For many years he delved in the literature of political economy at large, and equipped himself in the whole range of his subject. Not only the writings of contemporary economists, but those of earlier days, especially the English and French authors of the seventeenth and eighteenth centuries, and those of Ricardo's school, were thoroughly examined. It is characteristic of Professor Dunbar that notwithstanding the wide scope of his reading in the theoretic literature of political economy, he published virtually nothing on this phase of the subject; though the maturity of the conclusions derived from that reading are unmistakably evident in some of his essays on the recent phases of economic theory. He regarded these researches as essential to his equipment as a University teacher, partly also as preparation for the inquiries by which he hoped eventually to contribute to the world's stock of knowledge and thought.

The special subjects on which he planned to publish the results of research, and to which he gave most attention in the later years of his life, were public finance, taxation, currency, banking. It was to these that he had given most attention among the economic topics that presented themselves to him as editor of the Advertiser; it was to these that his own bent most attracted him. His range of information on them was remarkably wide. Here, again, his writings give but fragmentary indication of the extent of his attainments. He was familiar with the financial history and fiscal experiences of England and France quite as much as with those of the United States, to which his writings were chiefly devoted. And not only was he familiar with the facts; he was singularly skilful in interpreting them. All who had the pleasure of following his courses of instruction in the University

found before them the conclusions of a sagacious mind, furnished with ample information on every essential aspect of the situation. It was Professor Dunbar's undeviating habit to turn to the primary sources of information, — to the statutes, the official documents, the contemporary sources of knowledge. He was never content with information at second hand, and was frequently able to point out how the conclusions of authors of repute were overthrown by a careful comparison with the sources from which their conclusions should have been derived.

Professor Dunbar's writings, as already intimated, were comparatively scanty; they were certainly scanty as compared with what he was equipped to do. His little book on Banking, brief and unpretentious, is a model, and indeed well-nigh a classic, in its field. His essays on the financial history of the United States, published in the Quarterly Journal of Economies, are also models of their kind. Occasional comparisons, undertaken in these essays, with the financial experience of other countries, — as, for example, in the essay on Some Precedents followed by Alexander Hamilton, — give indication of the wide range of his researches. Similar evidence appears in essays on some recondite and little understood phases of economic history, such as those on the Bank of Amsterdam, on the Bank of Venice, and on Early Banking Schemes. Those who had the privilege of Professor Dunbar's intimate acquaintance knew that he had pushed his way into other obscure and difficult places also. He had given much attention to the history of the Assignats in France, and to the peculiarities in the course of depreciation during that remarkable episode in monetary history. On this subject he had collected, as was his habit, a store of contemporary material, and had planned at some time to present the results of his researches in published form. He had undertaken a minute and careful study of the financial administration of Alexander Hamilton, of which the results appeared in print only to a very slight extent. He had followed with equal thoroughness the history of banking operations in the United States, especially from the middle of the century to the present time; but here also failing strength and an untimely death prevented the execution of his matured plans.

No small part of Professor Dunbar's time and thought was given in the later years of his life to the Quarterly Journal of Economics. That Journal was established by Harvard University in 1886, Professor Dunbar being appointed its editor, and remaining in charge from 1886 to 1896. It was a very different editorial post from that which he had held on the Advertiser; but its duties were performed with no less

fidelity and skill. From the first a high standard was set. The Journal was to be a medium of communication for investigators, and took rank at once as one of the leading scholarly repertories on its subject. Space in it was sought by eminent writers the world over, and publication in its pages served as guarantee of a claim to the attention of the learned world. Professor Dunbar always looked back with just satisfaction on what he had here achieved, and found in it some solace for his inability to carry out his plans for independent publication.

Professor Dunbar was by nature reserved; always dignified; in conversation, happy in the intuitive selection of the right word; guarded in expressing an opinion, but sure to express a just one when his conclusions had been reached. His writings reflected these qualities. They are distinguished by a rounded stateliness of diction more sought for a generation ago than in our own day; dignified, yet never stilted, flowing, yet never affected. No more just and delightful tribute has been paid to a man in his own lifetime than is contained in Professor Dunbar's paper on President Eliot's Administration of Harvard University, published in the Harvard Graduates' Magazine (for June, 1894) at the close of the twenty-fifth year of President Eliot's administration. Equally sympathetic, and at the same time judicial and discriminating, are his memoirs, in the Proceedings of this Academy, of three men of very different types, — Henry C. Carey, Francis A. Walker, and E. W. Gurney.

It is a singular fact that Professor Dunbar wrote with hesitation, and often had to nerve himself anew to the task of literary composition. Notwithstanding many years of experience in rapid writing, he shrank from taking pen in hand; yet, when the first sentence was written, the others followed apparently with ease, and certainly in logical sequence and with an immediate happy choice of phrase. The present writer has been so fortunate as to examine some of the notes, memoranda, and unfinished manuscript left by his lamented colleague; and in the briefest and most fragmentary of these papers he has been repeatedly struck by the appositeness of the language, the instinctively systematic arrangement, the constant proof of clear and well ordered thought.

In personal intercourse with those who enjoyed his more intimate acquaintance, Professor Dunbar's habitual dignity and reserve were often broken by flashes of humor. He enjoyed keenly a good story, and saw the mirthful side of every subject. Often in solemn meetings the twinkle of his eye, perceptible only to those who knew him well, showed his appreciation of the oddities and idiosyncrasies of his contemporaries.

As is common with men whose sense of humor is strong, his affection was deep and lasting; and in the domestic circle the devotion which he gave and received was touching. His character, not less than his abilities and attainments, won from associates in varied walks of life an universal feeling of esteem and admiration.

F. W. TAUSSIG.

There have been no resignations during the year, but one Resident Fellow has abandoned his fellowship. One Resident Fellow, having removed from Massachusetts, has been elected to Associate Fellowship.

New members elected during the year are: Resident Fellows, 7; Associate Fellows, 9; Foreign Honorary Members, 9.

The roll of the Academy now includes 197 Resident Fellows, 96 Associate Fellows, and 70 Foreign Honorary Members.*

* By election, May 8, 1901, the roll is 198, 98, 74.

American Academy of Arts and Sciences.

OFFICERS AND COMMITTEES FOR 1900-1901.

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ALEXANDER AGASSIZ.

VICE-PRESIDENT.

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JOHN TROWBRIDGE.	ALPHEUS HYATT.	JAMES B. THAYER.

CORRESPONDING SECRETARY.

WILLIAM M. DAVIS.

RECORDING SECRETARY.

WILLIAM WATSON.

TREASURER.

FRANCIS BLAKE.

LIBRARIAN.

A. LAWRENCE ROTCH.

COUNCILLORS.

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THEODORE W. RICHARDS,	JOHN E. WOLFF,	WILLIAM EVERETT,
HARRY M. GOODWIN.	GEORGE H. PARKER.	A. LAWRENCE LOWELL.

COMMITTEE OF FINANCE.

ALEXANDER AGASSIZ, FRANCIS BLAKE, ELIOT C. CLARKE.

RUMFORD COMMITTEE.

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C. M. WARREN COMMITTEE.

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COMMITTEE ON THE LIBRARY.

A. LAWRENCE ROTCH, HENRY W. HAYNES, SAMUEL HENSHAW.

AUDITING COMMITTEE.

HENRY G. DENNY, WILLIAM L. RICHARDSON.

LIST

OF THE

FELLOWS AND FOREIGN HONORARY MEMBERS.

(Corrected to May 20, 1901.)

RESIDENT FELLOWS.—198.

(Number limited to two hundred.)

Class I.—*Mathematical and Physical Sciences.*—80.

Section I.—21.

Mathematics and Astronomy.

Solon I. Bailey,	Cambridge.
Maxime Bôcher,	Cambridge.
William E. Byerly,	Cambridge.
Seth C. Chandler,	Cambridge.
A. W. Duff,	Worcester.
Gustavus Hay,	Boston.
Theodore Lyman,	Brookline.
Henry Mitchell,	Nantucket.
William F. Osgood,	Cambridge.
James Mills Peirce,	Cambridge.
Edward C. Pickering,	Cambridge.
William H. Pickering,	Cambridge.
John Ritchie, Jr.,	Boston.
John D. Runkle,	Cambridge.
T. H. Safford,	Williamstown.
Edwin F. Sawyer,	Brighton.
Arthur Searle,	Cambridge.
William E. Story,	Worcester.
Henry Taber,	Worcester.
O. C. Wendell,	Cambridge.
P. S. Yendell,	Dorchester.

Section II.—21.

Physics.

A. Graham Bell,	Washington, D.C.
Clarence J. Blake,	Boston.
Francis Blake,	Weston.
Charles R. Cross,	Brookline.
Amos E. Dolbear,	Somerville.
H. M. Goodwin,	Roxbury.
Edwin H. Hall,	Cambridge.
Hammond V. Hayes,	Cambridge.
William L. Hooper,	Somerville.
William W. Jacques,	Newton.
Frank A. Laws,	Boston.
Henry Lefavour,	Williamstown.
T. C. Mendenhall,	Worcester.
Benjamin O. Peirce,	Cambridge.
A. Lawrence Rotch,	Boston.
Wallace C. Sabine,	Cambridge.
John S. Stone,	Boston.
Elihu Thomson,	Swampscott.
John Trowbridge,	Cambridge.
A. G. Webster,	Worcester.
Robert W. Willson,	Cambridge.

SECTION III. — 22.

Chemistry.

Samuel Cabot,	Boston.
Arthur M. Comey,	Cambridge.
James M. Crafts,	Boston.
Charles W. Eliot,	Cambridge.
Henry B. Hill,	Cambridge.
Charles L. Jackson,	Cambridge.
Walter L. Jennings,	Worcester.
Leonard P. Kinnicutt,	Worcester.
Charles F. Mabery,	Cleveland, O.
Arthur Michael,	Boston.
George D. Moore,	Worcester.
Charles E. Munroe,	Wash'gton, D.C.
John U. Nef,	Chicago, Ill.
Arthur A. Noyes,	Boston.
Robert H. Richards,	Boston.
Theodore W. Richards,	Cambridge.
Charles R. Sanger,	Cambridge.
Stephen P. Sharples,	Cambridge.
Francis H. Storer,	Boston.
Henry P. Talbot,	Newton.
Charles H. Wing,	Ledger, N. C.
Edward S. Wood,	Boston.

SECTION IV. — 16.

Technology and Engineering.

Eliot C. Clarke,	Boston.
Ira N. Hollis,	Cambridge.
L. M. Johnson,	Cambridge.
Gaetano Lanza,	Boston.
E. D. Leavitt,	Cambridge.
William R. Livermore,	Boston.
Hiram F. Mills,	Lowell.
Cecil H. Peabody,	Boston.
Alfred P. Rockwell,	Manchester.
Andrew H. Russell,	Wash'ton, D.C.
Peter Schwamb,	Arlington.
H. L. Smyth,	Cambridge.
Charles S. Storrow,	Boston.
George F. Swain,	Boston.
William Watson,	Boston.
Morrill Wyman,	Cambridge.

CLASS II. — *Natural and Physiological Sciences.* — 64.

SECTION I. — 13.

Geology, Mineralogy, and Physics of the Globe.

H. H. Clayton,	Milton.
Algernon Coolidge,	Boston.
William O. Crosby,	Boston.
William M. Davis,	Cambridge.
Benj. K. Emerson,	Amherst.
O. W. Huntington,	Newport, R. I.
Robert T. Jackson,	Cambridge.
William H. Niles,	Cambridge.
John E. Pillsbury,	Boston.
Nathaniel S. Shaler,	Cambridge.
Robert DeC. Ward,	Cambridge.
John E. Wolff,	Cambridge.
J. B. Woodworth,	Cambridge.

SECTION II. — 12.

Botany.

F. S. Collins,	Malden.
Geo. E. Davenport,	Medford.
William G. Farlow,	Cambridge.
Charles E. Faxon,	Boston.
Merritt L. Fernald,	Cambridge.
George L. Goodale,	Cambridge.
H. H. Hunnewell,	Wellesley.
John G. Jack,	Boston.
B. L. Robinson,	Cambridge.
Charles S. Sargent,	Brookline.
Arthur B. Seymour,	Cambridge.
Roland Thaxter,	Cambridge.

SECTION III. — 24.

Zoölogy and Physiology.

Alexander Agassiz,	Cambridge.
Robert Amory,	Boston.

James M. Barnard, Milton.
Henry P. Bowditch, Boston.
William Brewster, Cambridge.
Louis Cabot, Brookline.
William E. Castle, Cambridge.
Samuel F. Clarke, Williamstown.
W. T. Councilman, Boston.
Charles B. Davenport, Chicago, Ill.
Harold C. Ernst, Boston.
Edward G. Gardiner, Boston.
Samuel Henshaw, Cambridge.
Alpheus Hyatt, Cambridge.
John S. Kingsley, Somerville.
Edward L. Mark, Cambridge.
Charles S. Minot, Boston.
Edward S. Morse, Salem.
George H. Parker, Cambridge.
James J. Putnam, Boston.
Samuel H. Scudder, Cambridge.
William T. Sedgwick, Boston.
James C. White, Boston.
William M. Woodworth, Cambridge.

SECTION IV. — 15.

Medicine and Surgery.

Samuel L. Abbot, Boston.
Edward H. Bradford, Boston.
Arthur T. Cabot, Boston.
David W. Cheever, Boston.
Frank W. Draper, Boston.
Thomas Dwight, Boston.
Reginald H. Fitz, Boston.
Charles F. Folsom, Boston.
Frederick I. Knight, Boston.
Samuel J. Mixter, Boston.
W. L. Richardson, Boston.
Theobald Smith, Boston.
O. F. Wadsworth, Boston.
Henry P. Walcott, Cambridge.
John C. Warren, Boston.

CLASS III. — *Moral and Political Sciences.* — 54.

SECTION I. — 9.

Philosophy and Jurisprudence.

James B. Ames, Cambridge.
Horace Gray, Boston.
John C. Gray, Boston.
G. Stanley Hall, Worcester.
Geo. F. Hoar, Worcester.
Francis C. Lowell, Boston.
Josiah Royce, Cambridge.
Jeremiah Smith, Cambridge.
James B. Thayer, Cambridge.

SECTION II. — 21.

Philology and Archæology.

William S. Appleton, Boston.
Charles P. Bowditch, Boston.
Lucien Carr, Cambridge.
Franklin Carter, Williamstown.
Joseph T. Clarke, Boston.
Henry G. Denny, Boston.
William Everett, Quincy.
J. W. Fewkes, Washington.
William W. Goodwin, Cambridge.
Henry W. Haynes, Boston.
Charles R. Lanman, Cambridge.
David G. Lyon, Cambridge.
Bennett H. Nash, Boston.
Frederick W. Putnam, Cambridge.
Edward Robinson, Boston.
F. B. Stephenson, Boston.
Joseph H. Thayer, Cambridge.
Crawford H. Toy, Cambridge.
John W. White, Cambridge.
John H. Wright, Cambridge.
Edward J. Young, Waltham.

SECTION III. — 12.

Political Economy and History.

Charles F. Adams, Lincoln.
Edward Atkinson, Boston.
Andrew M. Davis, Cambridge.
Ephraim Emerton, Cambridge.
John Fiske, Cambridge.

A. C. Goodell,	Salem.
Henry C. Lodge,	Nahant.
A. Lawrence Lowell,	Boston.
James F. Rhodes,	Boston.
Denman W. Ross,	Gambridge.
Charles C. Smith,	Boston.
F. W. Taussig,	Cambridge.

SECTION IV. — 12.

Literature and the Fine Arts.

Francis Bartlett,	Boston.
John Bartlett,	Cambridge.
Arlo Bates,	Boston.
George S. Boutwell,	Groton.
J. Elliot Cabot,	Brookline.
T. W. Higginson,	Cambridge.
George L. Kittredge,	Cambridge.
Charles G. Loring,	Boston.
Percival Lowell,	Boston.
Charles Eliot Norton,	Cambridge.
Horace E. Scudder,	Cambridge.
Barrett Wendell,	Boston.

ASSOCIATE FELLOWS. — 98.

(Number limited to one hundred. Elected as vacancies occur.)

Class I. — *Mathematical and Physical Sciences.* — 37.

Section I. — 14.

Mathematics and Astronomy.

Edward E. Barnard,	Williams Bay, [Wis.
S. W. Burnham,	Chicago.
George Davidson,	San Francisco.
Fabian Franklin,	Baltimore.
Asaph Hall,	Cambridge, Mass.
George W. Hill,	W. Nyack, N.Y.
E. S. Holden,	Washington.
Emory McClintock,	Morristown, N.J.
E. H. Moore,	Chicago.
Simon Newcomb,	Washington.
Charles L. Poor,	Baltimore.
George M. Searle,	Washington.
J. N. Stockwell,	Cleveland, O.
Chas. A. Young,	Princeton, N. J.

Section II. — 7.

Physics.

Carl Barus,	Providence, R.I.
J. Willard Gibbs,	New Haven.
G. E. Hale,	Williams Bay.
S. P. Langley,	Washington.
A. A. Michelson,	Chicago.
Ogden N. Rood,	New York.
E. L. Nichols,	Ithaca.

Section III. — 8.

Chemistry.

T. M. Drown,	So. Bethlehem, Pa.
Wolcott Gibbs,	Newport, R.I.
Frank A. Gooch,	New Haven.
S. W. Johnson,	New Haven.
J. W. Mallet,	Charlottesville, Va.
E. W. Morley,	Cleveland, O.
J. M. Ordway,	New Orleans.
Ira Remsen,	Baltimore.

Section IV. — 8.

Technology and Engineering.

Henry L. Abbot,	New York.
Cyrus B. Comstock,	New York.
W. P. Craighill,	Charlestown, W. [Va.
John Fritz,	Bethlehem, Pa.
F. R. Hutton,	New York.
George S. Morison,	Chicago.
William Sellers,	Edgemoor, Del.
Robt. S. Woodward,	New York.

Class II. — *Natural and Physiological Sciences.* — 34.

Section I. — 14.

Geology, Mineralogy, and Physics of the Globe.

Cleveland Abbe,	Washington.
George J. Brush,	New Haven.
T. C. Chamberlin,	Chicago.
Edward S. Dana,	New Haven.
Walter G. Davis,	Cordova, Arg.
G. K. Gilbert,	Washington.
Clarence King,	New York.
Joseph LeConte,	Berkeley, Cal.
J. Peter Lesley,	Milton, Mass.
S. L. Penfield,	New Haven.
J. W. Powell,	Washington.
R. Pumpelly,	Newport, R.I.
A. R. C. Selwyn,	Vancouver.
Charles D. Walcott,	Washington.

Section II. — 6.

Botany.

L. H. Bailey,	Ithaca.
D. H. Campbell,	Palo Alto, Cal.
J. M. Coulter,	Chicago.
C. G. Pringle,	Charlotte, Vt.
John D. Smith,	Baltimore.
W. Trelease,	St. Louis.

Section III. — 8.

Zoölogy and Physiology.

Joel A. Allen,	New York.
W. K. Brooks,	Lake Roland, Md.
F. P. Mall,	Baltimore.
S. Weir Mitchell,	Philadelphia.
H. F. Osborn,	New York.
A. S. Packard,	Providence, R.I.
A. E. Verrill,	New Haven.
C. O. Whitman,	Chicago.

Section IV. — 6.

Medicine and Surgery.

John S. Billings,	New York.
W. S. Halsted,	Baltimore.
W. W. Keen,	Philadelphia.
William Osler,	Baltimore.
Wm. H. Welch,	Baltimore.
H. C. Wood,	Philadelphia.

Class III. — *Moral and Political Sciences.* — 27.

Section I. — 6.

Philosophy and Jurisprudence.

James C. Carter,	New York.
Joseph H. Choate,	New York.
Melville W. Fuller,	Washington.
William W. Howe,	New Orleans.
Charles S. Peirce,	Milford, Pa.
T. R. Pynchon,	Hartford, Conn.

Section II. — 7.

Philology and Archæology.

Timothy Dwight,	New Haven.
B. L. Gildersleeve,	Baltimore.
D. C. Gilman,	Baltimore.
T. R. Lounsbury,	New Haven.
Rufus B. Richardson,	Athens.
Thomas D. Seymour,	New Haven.
A. D. White,	Ithaca, N.Y.

Section III. — 6.

Political Economy and History.

Henry Adams,	Washington.
G. P. Fisher,	New Haven.
H. E. von Holst,	Chicago.
Henry C. Lea,	Philadelphia.
Henry M. Stevens,	Ithaca.
W. G. Sumner,	New Haven.

Section IV. — 8.

Literature and the Fine Arts.

James B. Angell,	Ann Arbor, Mich.
L. P. di Cesnola,	New York.
H. H. Furness,	Wallingford, Pa.
R. S. Greenough,	Florence.
Augustus St. Gaudens,	New York.
John S. Sargent,	London.
E. C. Stedman,	Bronxville, N.
W. R. Ware,	New York.

FOREIGN HONORARY MEM

(Number limited to seventy-five. Elected as vaca

Class I. — *Mathematical and Physical S*

Section I. — 7.

Mathematics and Astronomy.

Arthur Auwers,	Berlin.
George H. Darwin,	Cambridge.
H. A. E. A. Faye,	Paris.
Sir William Huggins,	London.
H. Poincaré,	Paris.
Otto Struve,	Karlsruhe.
H. C. Vogel,	Potsdam.

Section II. — 6.

Physics.

Ludwig Boltzmann,	Vienna.
A. Cornu,	Paris.
Oliver Heaviside,	Newton Abbot.
F. Kohlrausch,	Berlin.
Lord Rayleigh,	Witham.
Sir G. G. Stokes, Bart.,	Cambridge.

Secti

C

Adolf Baeyer,
Marcellin Bert
J. H. van't Ho
D. Mendeleeff,
Sir H. E. Rosc
Julius Thomse

Secti

Technology

Sir Benjamin B
Lord Kelvin,
Maurice Lévy,
H. Müller-Bres
William C. Un

Class II. — *Natural and Physiological Sc*

Section I. — 7.

Geology, Mineralogy, and Physics of the Globe.

Sir Archibald Geikie,	London.
Albert Heim,	Zurich.
Sir John Murray,	Edinburgh.
A. E. Nordenskiöld,	Stockholm.
Freih. v. Richthofen,	Berlin.
Henry C. Sorby,	Sheffield.
Heinrich Wild,	Zurich.

Secti

I

E. Bornet,
A. Engler,
Sir Joseph D. I
W. Pfeffer,
H. Graf zu S
Laubach,
Eduard Strasb